PB81-118911

Evaluation of Ozone Calibration Procedures

(U.S.) Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Nov 80

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA 600/4-80-050

2.

3. RECIPIENT'S ACCESSION NO.
PB81 118911

4. TITLE AND SUBTITLE
EVALUATION OF OZONE CALIBRATION PROCEDURES

5. REPORT DATE

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Quality Assurance Division
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Monitoring Systems Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final Report

14. SPONSORING AGENCY CODE
EPA 600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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This publication summarizes the evaluation effort of the U.S. Environmental Protection Agency to select an alternate calibration procedure. Each method was subjected to a preliminary investigation to review the procedural descriptions and to assess the critical performance parameters. Variability studies were subsequently conducted to estimate the precision and accuracy of ozone calibrations using the four methods. The results of these studies were then compared. The ultraviolet photometry procedure was determined to be the most dependable and accurate and was designated the replacement procedure.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Calibration	Ozone	43F
UV Photometry	Nitric oxide	68A
Gas Phase Titration	Nitrogen dioxide	
Iodometry	Potassium iodide	
Ozone analyzers		

18. DISTRIBUTION STATEMENT RELEASE UNLIMITED	**19. SECURITY CLASS** *(This Report)* UNCLASSIFIED	**21. NO. OF PAGES** 227
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	**22. PRICE**

PB81-118911

EPA-600/4-80-050
November 1980

EVALUATION OF
OZONE
CALIBRATION PROCEDURES

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

The work covered in this report details the Environmental Monitoring System Laboratory's efforts to provide improved methodology for compliance monitoring. The calibration procedure for the reference method for the measurement of ozone in the atmosphere was known to be variable and in some cases inaccurate. The Environmental Monitoring Systems Laboratory investigated four calibration procedures with the intent of replacing the old neutral buffered potassium iodide calibration procedure. The work reported here was a major factor in the ultimate replacement of the neutral buffered potassium iodide procedure with the ultraviolet photometric calibration procedure.

T. R. Hauser

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This report summarizes the evaluation effort of the U.S. Environmental Protection Agency to select an alternate calibration procedure. Each method was subjected to a preliminary investigation to review the procedural descriptions and to assess the critical performance parameters. Variability studies were subsequently conducted to estimate the precision and accuracy of ozone calibrations using the four methods. The results of these studies were then compared. The ultraviolet photometry procedure was determined to be the most dependable and accurate and was designated the replacement procedure.

Included in the appendices to this report are the four tentative calibration procedures that were evaluated. Pertinent data on the apparatus used, the individual volunteers, and the variability data extrapolated from test results are also provided in the appendices.

EPA-287 (Cin.)
(4-76)

CONTENTS

Foreword iii
Abstract iv
Figures vii
Tables ix
Acknowledgments xiii

1. Introduction 1
2. Conclusions 4
3. Ultraviolet Photometry 6
    Introduction 6
    Preliminary investigation 7
    Variability study 18
4. Gas Phase Titration with Excess Nitric Oxide 28
    Introduction 28
    Preliminary investigation 28
    Variability study 43
5. Gas Phase Titration with Excess Ozone 59
    Introduction 59
    Preliminary investigation 60
    Variability study 66
    Additional study 78
6. Boric Acid-Potassium Iodide 83
    Introduction 83
    Preliminary investigation 84
    Variability study 99

References 111

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA: OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
6-1/2"
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

CONTENTS (continued)

Appendices

A. Tentative calibration procedure using ultraviolet photometry 113
B. Tentative calibration procedure using gas phase titration with excess nitric oxide 124
C. Tentative calibration procedure using gas phase titration with excess ozone 137
D. Tentative calibration procedure using boric acid-potassium iodide (BAKI) 148
E. Tentative calibration procedure using boric acid-potassium iodide (BAKI) (revised) 161
F. Volunteers and volunteer ozone calibration systems 175
G. Test laboratory preparation for variability studies 185
H. Miscellaneous 197
I. Analysis of variance 202

6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

FIGURES

Number		Page
1	Dasibi UV photometry system	8
2	Comparison of Dasibi 1141 with Dasibi 1365 used by NBS as a transfer standard	12
3	Comparison of Dasibi 1141 with the NBS photometer . . .	13
4	Comparison of Dasibi photometer with GPT-NO	16
5	Diagram of reference system	20
6	Diagram of a typical GPT calibration system	29
7	Diagram of calibration apparatus using NO_2 permeation device	31
8	Completeness of reaction versus NO consumed at various dynamic parameter specifications	33
9	Completeness of reaction versus NO consumed at various dynamic parameter specifications	34
10	Completeness of reaction versus NO consumed at various dynamic parameter specifications	35
11	Diagram of control GPT system	45
12	Diagram of NO_2 permeation system	46
13	Least squares linear plot of $[O_3]_{GPT-O_3}:[O_3]_{UV}$ ratio versus P_R for control GPT system	82
14	Least squares linear plot of $[O_3]_{GPT-O_3}:[O_3]_{UV}$ ratio versus P_R for Bendix GPT system	82
15	Diagram of O_3 test generation and distribution system .	86
16	Comparison of BAKI and Dasibi O_3 measurements	96
17	Diagram of reference system	101
18	Hastings mass flowmeter calibration curve	102

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

FIGURES (continued)

Number		Page
A-1	Schematic diagram of a typical UV photometric calibration system	122
A-2	Schematic diagram of a typical UV photometric calibration system (Option 1)	123
B-1	Schematic diagram of a typical GPT calibration system	136
C-1	Schematic diagram of a typical GPT calibration system	147
D-1	Schematic diagram of a typical O_3 calibration system	159
D-2	Diagram of KI sampling train	160
E-1	Schematic diagram of a typical O_3 calibration system	173
E-2	Diagram of KI sampling train	174
G-1	Initial O_3 calibration curve (B1)	194
G-2	Initial O_3 calibration curve (B2)	194
G-3	Initial O_3 calibration curve (B3)	195
G-4	Initial NO calibration curve	195
G-5	Initial NO_2 calibration curve	196

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLES

Number Page

1 Comparison of O_3 Calibration Variability 4
2 Comparison of UV Photometry with GPT-NO 15
3 Comparison of Dasibi 1141 and Dasibi 1143 Over Time. . 17
4 Regression Constants for UV Calibration Runs (UV Photometer) 23
5 Regression Constants for UV Calibration Runs (UV Monitor) 24
6 Variability of UV Photometric O_3 Calibrations 25
7 GPT-NO O_3 Analyzer Calibration Using Option 1 (Test No. 1) 37
8 GPT-NO O_3 Analyzer Calibration Using Option 1 (Test No. 2) 38
9 GPT-NO O_3 Analyzer Calibration Using Option 2. 39
10 Comparison of $[O_3]_{GPT-NO}:[O_3]_{UV}$ Ratios 40
11 Comparison of $[NO_2]_{PD}$ Versus $[NO_2]_{GPT}$ 41
12 O_3 Generator Output Stability 42
13 Regression Constants for GPT-NO Control System Calibration Runs 49
14 Regression Constants for GPT-NO Volunteer System Calibration Runs 50
15 Variability of GPT-NO O_3 Calibrations. 51
16 GPT-NO Supplemental Measurements and Corrected O_3 Calibration Slopes for Volunteer Systems 52
17 Regression Slopes for Change in NO (Volunteer GPT) Versus NO_2 (Reference Measurement) 54
18 Variability of GPT-NO NO_2 Calibrations 56

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MAGE AREA
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AND ILLUS-
TRATIONS
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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLES (continued)

Number Page

19 Verification of Dynamic Parameter and O_3 Reduction Specifications and Comparison of O_3 by GPT-O_3 and UV Photometry . . . 63
20 $[O_3]_{GPT-O_3}$ Assays Using 700 and 2000 CM^3 Reaction Chambers. 65
21 Regression Constants for GPT-O_3 Control System Calibration Runs . . . 71
22 Regression Constants for GPT-O_3 Volunteer System Calibration Runs . . . 72
23 GPT-O_3 Supplemental Measurements and Corrected Calibration Slopes for Volunteer Systems . . . 73
24 Variability of GPT-O_3 Ozone Calibrations . . . 74
25 $[NO]_{OUT}$ and $[NO]_{Residual}$ Measurements from Volunteer System Calibrations . . . 76
26 $[O_3]_{GPT-O_3}:[O_3]_{UV}$ Ratios Versus P_R for Control GPT System . . . 79
27 $[O_3]_{GPT-O_3}:[O_3]_{UV}$ Ratios Versus P_R for Bendix GPT System . 80
28 Components of KI Sampling Trains . . . 87
29 Reagents for BAKI Procedure . . . 89
30 Spectrophotometers . . . 90
31 Manifold Integrity Test Results . . . 91
32 KI Calibration Data . . . 93
33 BAKI O_3 Concentrations and Corresponding Dasibi O_3 Concentrations . . . 95
34 Regression Data for BAKI O_3 Measurements . . . 97
35 BAKI O_3 Measurements - Zero Air . . . 98
36 Regression Constants for BAKI O_3 Calibration Runs . . . 107

BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLES (continued)

Number — Page

37 Variability of BAKI O_3 Calibrations 108
G-1 Dasibi Photometer Set-Up 186
G-2 Comparison of Dasibi Photometer with QAD Photometer 186
G-3 Photometer Comparison #1 187
G-4 Photometer Comparison #2 187
G-5 Photometer Comparison #3 188
G-6 O_3 Analyzer Set-Up 188
G-7 O_3 Analyzer Calibration 189
G-8 O_3 Generator Output 190
G-9 Bendix NO_x Analyzer (S/N 30307-28) 191
G-10 Bendix NO_x Analyzer (S/N 29671-8) 191
G-11 Bendix NO_x Analyzer (S/N 30307-7) 192
G-12 Bendix NO_x Analyzer (S/N 30307-29) 192
G-13 Certification of Flow Measurement Devices Against Two Primary Standards 193
I-1 Analysis of Variance for All UV Calibrations 203
I-2 Analysis of Variance for Dasibi Monitors 203
I-3 Analysis of Variance for Dasibi Photometers 204
I-4 Analysis of Variance for All UV Calibrations (Corrected to Reference Photometer) 204
I-5 Analysis of Variance for Dasibi Monitors (Corrected to Reference Photometer) 205
I-6 Analysis of Variance for Dasibi Photometers (Corrected to Reference Photometer) 205
I-7 Analysis of Variance for Control GPT-NO System 206
I-8 Analysis of Variance for Volunteer GPT-NO Systems 206

BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLES (continued)

Number **Page**

I-9 Analysis of Variance for Volunteer GPT-NO Systems (Corrected for Reference Flow and Cylinder Assay) . . . 207
I-10 Analysis of Variance for Control GPT-NO System 207
I-11 Analysis of Variance for Volunteer GPT-NO Systems 208
I-12 Analysis of Variance for Volunteer GPT-NO Systems (Corrected for Reference Flow and Cylinder Assay) . . . 208
I-13 Analysis of Variance for Control GPT-O_3 System 209
I-14 Analysis of Variance for Control GPT-O_3 System (Slopes Forced Through Zero) 209
I-15 Analysis of Variance for Volunteer GPT-O_3 Systems 210
I-16 Analysis of Variance for Volunteer GPT-O_3 Systems (Slopes Forced Through Zero) 210
I-17 Analysis of Variance for Volunteer GPT-O_3 Systems (Corrected for Reference Flow and Cylinder Assay) . . . 211
I-18 Analysis of Variance for BAKI Calibrations at RTP 211
I-19 Analysis of Variance for BAKI Calibrations at RTP (Slopes Forced Through Zero) 212
I-20 Analysis of Variance for BAKI Calibrations at RTP (Corrected for I_2 Molar Absorptivity) 212
I-21 Analysis of Variance for All BAKI Calibrations 213

BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

ACKNOWLEDGMENTS

The authors would like to express appreciation to all of the volunteers who participated in the variability studies. The authors would like to thank Mr. Larry J. Purdue, Mr. Frank F. McElroy, Mr. Jack C. Suggs, and Dr. E. Carol Ellis who participated with the authors in this project as members of the Ozone Working Group. The authors would also like to thank Ms. Katherine A. Powers who typed the manuscript.

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EPA-287 (Cin.)
(4-76)

SECTION 1

INTRODUCTION

On October 6, 1976, the U.S. Environmental Protection Agency (EPA) published an advance notice of proposed rulemaking in the Federal Register (1) citing evidence that the calibration procedure previously specified for EPA reference methods for the determination of photochemical oxidants in the atmosphere (2) was subject to significant error and variability. The notice indicated EPA's intentions to evaluate alternative calibration procedures prior to proposing amendments to replace or revise the existing procedure.

Four candidate procedures were considered promising replacements for the 1 percent neutral buffered potassium iodide (NBKI) procedure then currently in use: gas phase titration with excess nitric oxide (GPT-NO), gas phase titration with excess ozone (GPT-O_3), ultraviolet (UV) photometry, and an improved potassium iodide technique using a boric acid buffered potassium iodide reagent (BAKI). Each of these procedures had been demonstrated to give results of adequate precision and accuracy under ideal conditions before being considered as candidates for replacing the NBKI procedure.

Each of the candidate procedures was then evaluated by an internal EPA working group consisting of members from the Environmental Monitoring Systems Laboratory (EMSL) and the Environmental Sciences Research Laboratory (ESRL) of Research Triangle Park (RTP), North Carolina. All procedures were subjected to preliminary evaluations in order to review the procedural descriptions and to assess critical performance parameters. Variability studies were subsequently conducted to estimate the precision and accuracy of the calibrations. The information from these studies was used to assess the relative performance of each procedure and ultimately to select the most appropriate procedure for calibrating O_3 reference methods.

EPA-287 (Cin.)
(4-76)

The variability studies were conducted using volunteers from within and outside of EPA, selected to represent technicians likely to use the procedures at state and local air pollution agencies. Volunteers were provided with a description of the method and asked to obtain the necessary calibration apparatus and to familiarize themselves with the procedure. The volunteers were then brought to a test laboratory where they generated O_3 concentration standards which were quantitatively compared to a highly stable reference system. This system consisted of three chemiluminescence O_3 analyzers, a UV photometer, an O_3 generation and dilution system, and a dynamic AC line voltage regulator. In the case of the GPT methods, volunteers also generated O_3 concentration standards with a common or control GPT system in order to estimate the operator contribution to the total variability of these methods.

A least squares linear regression equation was determined for each set of O_3 atmospheres generated. Each regression equation was in the form of:

$$O_3 \text{ (Volunteer)} = B_1 O_3 \text{ (Reference)} + B_2 \qquad (1\text{-}1)$$

An analysis of variance was then performed on the regression slopes using the following model to estimate the precision (variability) and accuracy (bias) of the method:

$$B_{ij} = \mu + T_i + E_{ij} \qquad (1\text{-}2)$$

where: B_{ij} = slope from the j^{th} calibration by the i^{th} treatment
μ = true mean slope for O_3 calibrations using a given method
T_i = i^{th} treatment effect, variability = σ_t, mean = 0
E_{ij} = error effect, variability = σ_e, mean = 0

The error (or bias) associated with the calibration system (operator and equipment) is represented by T_i; the error (or bias) associated with chance (experimental error) is represented by E_{ij}. Treatment variability

EPA-287 (Cin.)
(4-76)

(σ_t) is that component of the total variability (σ_{tot}) attributable to differences in the calibration systems (operator and equipment). Error variability (σ_e) is that component of the total variability attributable to chance (experimental error).

The reproducibility of a given method was defined as the 95 percent confidence interval of the difference in the slopes of two calibrations performed by different operators using different calibration systems on different days and was estimated by:

$$\text{Reproducibility} \leq 1.96 \sqrt{2\,\sigma^2_{tot}} \qquad (1\text{-}3)$$

This report is a compilation of both the preliminary investigations and the variability studies conducted for each of the four methods. In addition, pertinent data on the various apparatus used, the individual volunteers, and the variability data extrapolated from test results are provided in the appendices to this text.

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SECTION 2

CONCLUSIONS

The results from the preliminary investigations indicated that all four calibration procedures were suitable for the calibration of O_3 reference methods and should be subjected to further evaluation in variability studies.

The results from the four variability studies are summarized in Table 1. These data indicate that the UV photometric calibration procedure is the least variable of the four evaluated procedures (reproducibility 3.4 percent), and that UV photometers employed for calibration purposes have no significant bias (mean slope 1.0037). The estimated bias value for the UV photometers does not of itself confirm the accuracy of UV photometry, since the reference system for this particular study was also based on UV photometry. However, its accuracy for measuring O_3 concentrations is confirmed by its direct relationship to a well established O_3 absorption coefficient as well as comparisons of independent UV photometers that showed agreement within ± 1.5 percent (3).

TABLE 1. COMPARISON OF O_3 CALIBRATION VARIABILITY

Procedure	N*	Mean slope	σ_{tot}	Reproducibility
UV photometry	10	1.0037	0.0123	0.0341
GPT-NO	10	1.0742	0.0383	0.1062
GPT-O_3	9	1.0787	0.0669	0.1854
BAKI	12	0.9865	0.0557	0.1544

*N = number of participating volunteers

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The two GPT procedures proved more variable than the UV photometric procedure and also yielded an average bias of 7 to 8 percent with respect to the UV photometric reference system. Experiments conducted with both volunteer and control (common) GPT systems indicated that an important component of the total variability of GPT calibrations was due to differences in calibration apparatus. However, variability effects due to volunteers were found to be negligible. Preliminary investigations of the GPT procedures also revealed a positive bias with respect to UV photometry.

The BAKI procedure was also considerably more variable than the UV photometric technique. No significant bias was found when this procedure was compared to UV photometry.

Based on results from the four evaluations, the UV photometric procedure was the least variable and most accurate. Accordingly, this procedure has been proposed and promulgated by EPA as the replacement for the NBKI procedure for calibration of O_3 reference methods (4).

Independent use of the BAKI procedure for the direct calibration of O_3 reference methods is allowed for a 18-month transition period to permit agencies to adopt the new UV calibration procedure. The use of transfer standards is also allowed, provided they meet certain performance specifications and are certified against the UV photometric procedure. Transfer standards for O_3 can include procedural techniques such as BAKI and GPT, as well as devices such as O_3 analyzers and stable O_3 generators.

The GPT-NO procedure evaluated in this study is one of the procedures prescribed by EPA for the calibration of reference methods for the measurement of nitrogen dioxide (NO_2) in the atmosphere (5). The accuracy and precision of this procedure for NO_2 calibrations was also investigated during the course of the present study. The GPT-NO procedure, when used for NO_2 calibrations, showed no significant bias (when quantitatively compared to a reference system based on a National Bureau of Standards NO_2 Standard Reference Material), and a reproducibility of less than 7 percent, 95 percent of the time.

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SECTION 3

ULTRAVIOLET PHOTOMETRY

INTRODUCTION

One of the calibration techniques investigated by EPA to replace the NBKI method was absorption photometry (UV photometry). Absorption photometry is an attractive technique because only a small number of a sample's physical parameters need to be measured. This procedure is based on the photometric assay of O_3 concentrations in a dynamic flow system. Ozone readily lends itself to measurement by absorption photometry due to its strong absorption band in the 200 to 300 nm range. Since the peak of this band almost coincides with the 254 nm line of a low pressure mercury (Hg) discharge lamp, the concentration of O_3 in an absorption cell can be determined from a measurement of the amount of 254 nm light absorbed by the sample. The concentration of O_3 is then related to absorbed light by the Beer-Lambert absorption law:

$$\text{Transmittance (T)} = \frac{I}{I_o} = e^{-\alpha c \ell} \qquad (3\text{-}1)$$

where: I = the intensity of light which passes through the cell and is sensed by the detector when the cell contains an O_3 sample

I_o = the intensity of light which passes through the cell and is sensed by the detector when the cell contains zero air

α = absorption coefficient of O_3 at 254 nm = 308 ± 4 $\text{atm}^{-1}\ \text{cm}^{-1}$ at 0° C and 760 torr

c = O_3 concentration in atmosphere

ℓ = optical path length in cm.

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PRELIMINARY INVESTIGATION

The general performance of the UV photometric technique has been investigated independently by several workers (3,6,7,8). An investigation to evaluate the performance of the UV photometric procedure for calibrating O_3 monitors was conducted by the Atmospheric Chemistry and Physics Division (ACPD), ESRL, EPA/RTP. The investigation included examination of the operation of a commercially available photometric O_3 analyzer (Dasibi Model 1003-AH) and evaluation of measurements made with modified Dasibi analyzers.

A Dasibi O_3 analyzer proves to be a convenient instrument for evaluating the photometric O_3 calibration procedure. The Dasibi instrument uses a low-pressure mercury discharge lamp for its light source. The 185 nm radiation from the mercury lamp is blocked by means of a Vycor shield surrounding the lamp. The solar-blind vacuum photodiode detectors do not respond to radiation wavelengths greater than 300 nm. This source-detector combination produces an effective monochromatic photometer operating at the 254 nm Hg line.

The Dasibi is a two-channel photometer system (see Figure 1). One detector (sample channel) monitors the intensity of 254 nm radiation passing through the absorption cell. A second detector (control channel) positioned near the UV source views a fraction of the 254 nm radiation. The control channel functions as an energy monitor and is employed to compensate for changes in source intensity. The electrometers employed in the Dasibi instrument are current-to-frequency converters. Digitized signals are fed into a patented counting system. This counting system also controls a solenoid valve allowing either zero air or ozonized air to pass through the absorption cell.

A Dasibi O_3 analyzer can easily be modified to operate as a photometer to measure the relative transmittances of two gas samples at 254 nm. If one gas sample is zero air and the second sample contains O_3 in zero air, the concentration of O_3 in the latter sample may be calculated from the measured transmittance of the sample, the known absorbtivity of O_3 at 254 nm, and the optical pathlength.

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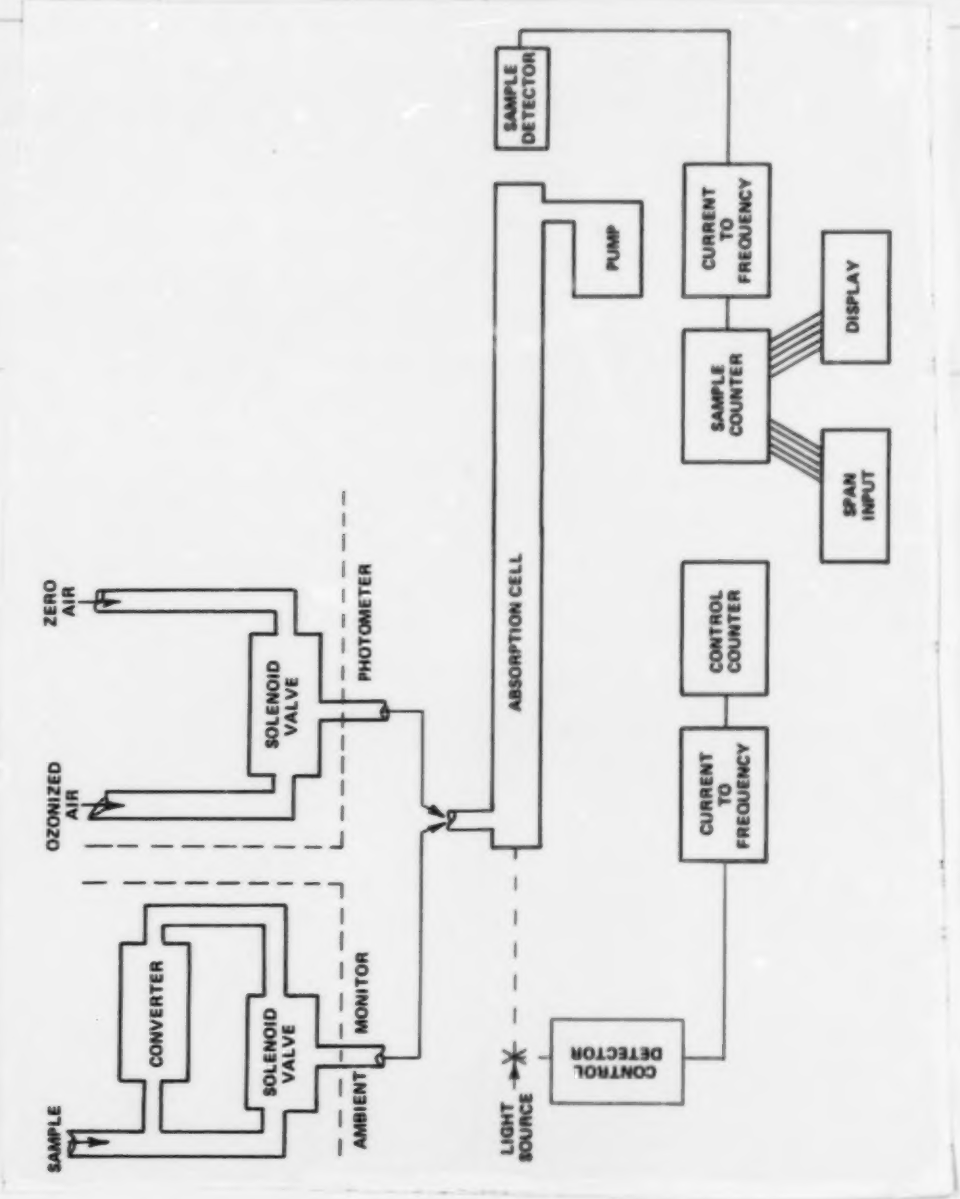
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SAMPLE COUNTER
DISPLAY
CURRENT TO FREQUENCY

Figure 1. Dasibi UV photometry system.

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

The Dasibi photometer used for O_3 calibrations uses a linear approximation of Equation 3-1 to convert the measured transmittance to a concentration. Use of the linear approximation of the absorption law results in only small errors for O_3 concentrations less than 1 ppm. For example, at 1 ppm there is 1.0 percent error and the error decreases at lower concentrations.

The major advantages of the photometric technique include ease of use, the obviation of chemical standards or reagents, and the relatively short calibration time required.

Experimental

Test Atmosphere Generation--

Ozone was generated by UV irradiation of clean air passing through a quartz tube.

Test Atmosphere Measurements--

Two Dasibi photometers were used for the bulk of the work, S/N 1141 and S/N 1143. The instruments were normally set up with a span number of 50730, which assumes an absorptivity of 308 atm^{-1} cm^{-1} (273° K, 760 torr), a pathlength of 71 cm, a temperature of 300° K and a pressure of 752 torr for the system. The Dasibis were operated without top covers, which had previously caused the temperature in the absorption cells to increase approximately 10° C. Flow rate through the instruments was nominally 2 l/min.

Dasibi Modifications--

Both Dasibis were modified at the start of the investigation. In general, the modifications concern three main features:

- The O_3 converter was removed from the instrument and zero air was diverted from upstream of the O_3 generation system and brought to the reference side of the instrument's solenoid valve.

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

- The sample channel counter was allowed to count below numerical zero.

- The solenoid valve was relocated a few inches away from the absorption cell.

Results and Discussions

Photometer Zero Air Supply--

During the course of the studies, it became evident that photometers are quite sensitive to the quality of zero air used. For instance, if air for the reference part of the instrument cycle is obtained from one air supply and air for the sample from another air supply, the difference in transmittance of the two air samples may vary by an amount corresponding to 100 ppb or more of O_3. Thus, it is crucial that the reference air be a portion of the same air that is passed through the O_3 generator. In most experiments, the reference air was obtained by simply dividing the air supply upstream of the generator flow control device and making part of it available to the instrument for the reference part of the cycle.

If the air stream contains particles (perhaps from a charcoal scrubber) the photometer may not zero properly, because the calibration system may remove more particles from the sample air stream than are removed from the reference air stream. In this case, the instrument zeroes below numerical zero on the display. When the instruments do not zero properly, the most likely source of the problem is the air supply.

Comparison of Dasibi Photometer with National Bureau of Standards Photometer--

Direct and indirect comparisons were made using an EPA/RTP Dasibi photometer (S/N 1141) and a 3-meter photometer located at the National Bureau of Standards (NBS) in Gaithersburg, Maryland. Comparisons of EPA and NBS photometers were obtained by simultaneously analyzing an O_3 test atmosphere with both photometers and performing a linear regression on the resulting O_3 concentrations.

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EPA-287 (Cin.)
(4-76)

The indirect comparison of Dasibi 1141 with the NBS photometer was carried out by using an unmodified NBS Dasibi (S/N 1365) as a transfer standard. Dasibi 1365 was operated using a span number of 68600 at a pressure of 754 torr and an absorption cell temperature of 40° C. The displayed numbers from this instrument must be reduced by the ratio of the theoretical span number to the actual span number used during measurement of the O_3 concentrations. The theoretical span number is calculated as:

$$\text{Theoretical span} = \frac{10^{9}}{134 \times 2.30259 \times 71} \times \frac{313}{273} \times \frac{760}{754} = 52752 \qquad (3\text{-}2)$$

The correction factor is then calculated as:

$$\text{Correction factor} = \frac{52752}{68600} = 0.7690 \qquad (3\text{-}3)$$

Multiplying the displayed values of the Dasibi 1365 by this correction factor yields the relationship:

$$O_3 \text{ (Dasibi 1365)} = 0.984\ O_3 \text{ (Dasibi 1141)} \qquad (3\text{-}4)$$

The comparison of Dasibi 1365 (corrected to theoretical span number) with Dasibi 1141 is shown in Figure 2.

Experiments conducted at NBS show that after the above correction, Dasibi 1365 indicates 2 percent less O_3 than the NBS photometer. Accepting Dasibi 1365 as a transfer standard yields:

$$O_3 \text{ (NBS photometer)} = 1.02\ O_3 \text{ (Dasibi 1365)} = 1.02 \times 0.984\ O_3 \text{ (Dasibi 1141)}$$

$$O_3 \text{ (NBS photometer)} = 1.003\ O_3 \text{ (Dasibi 1141)} \qquad (3\text{-}5)$$

Dasibi 1141 was then directly compared with the NBS photometer (Figure 3). The direct comparison yielded the following relationship:

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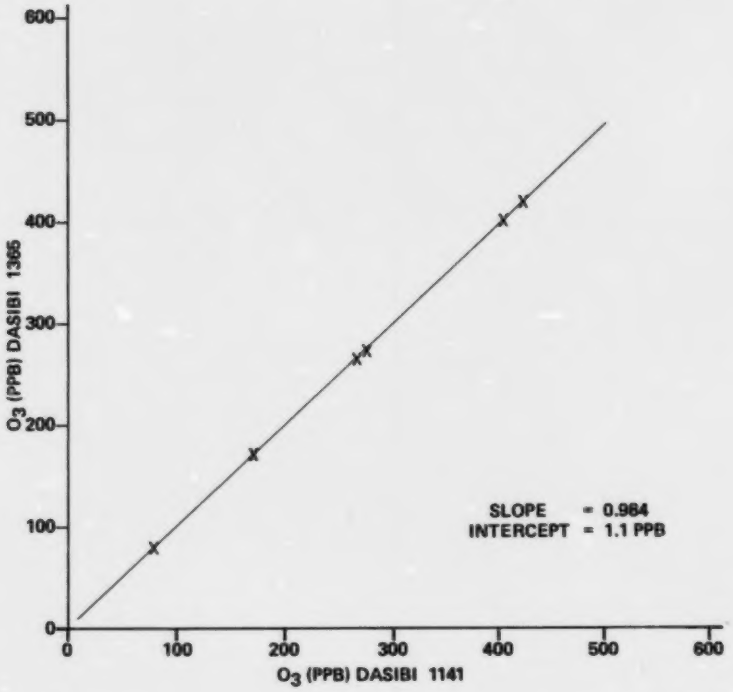

Figure 2. Comparison of Dasibi 1141 with Dasibi 1365 used by NBS as a transfer standard.

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EPA-287 (Cin.)
(4-76)

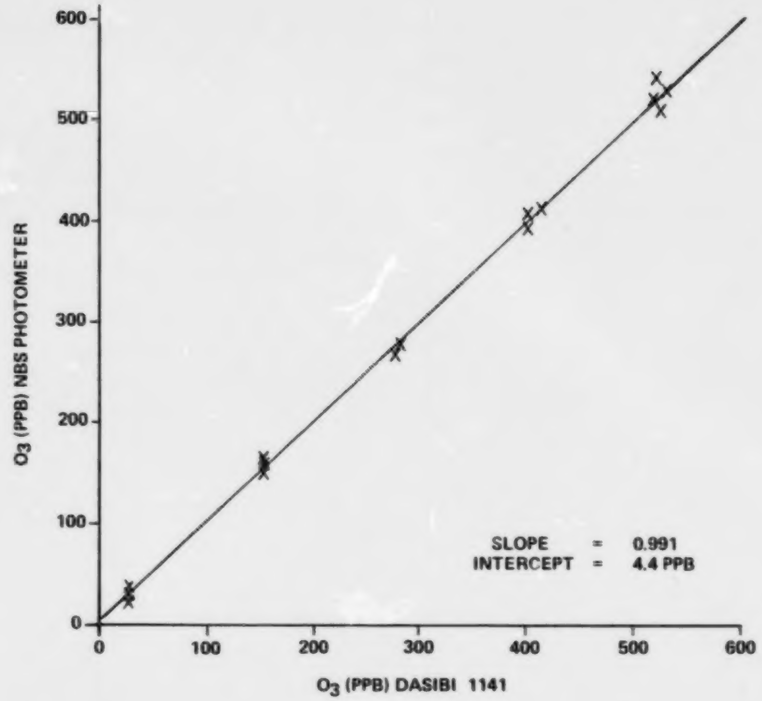

Figure 3. Comparison of Dasibi 1141 with the NBS photometer.

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EPA-287 (Cin.)
(4-76)

$$O_3 \text{ (NBS photometer)} = 0.991\ O_3 \text{ (Dasibi 1141)} + 4.4 \text{ ppb} \qquad (3\text{-}6)$$

The slopes from the direct and indirect comparisons differed by less than 2 percent.

The rather large intercept in the direct comparison is due to three anomalously high points (one at 25 ppb and two at 150 ppb). If these three points are dropped from the analysis, the 15 remaining points yield:

$$O_3 \text{ (NBS photometer)} = 1.003\ O_3 \text{ (Dasibi 1141)} - 1.75 \text{ ppb} \qquad (3\text{-}7)$$

The slope of this corrected comparison is then the same as that obtained in the indirect comparison. Even without omitting the anomalous data points, the comparison between the NBS and EPA photometers is excellent.

Comparison of Ultraviolet Photometry with Gas Phase Titration with Excess Nitric Oxide--

Several comparisons were made between UV photometric and GPT-NO ozone calibrations. The comparisons were obtained by generating O_3 test atmospheres by a GPT-NO procedure similar to that described in Appendix B of this report and assaying them with the Dasibi (S/N 1141) photometer. Comparisons were made between (1) a Dasibi photometer and a unitized GPT system; (2) a Dasibi photometer and a commercial O_3 calibrator using GPT; and (3) a Dasibi photometer and a homemade modular GPT system. Linear regression analyses were then performed on the resulting O_3 concentrations and the results are shown in Table 2. All three comparisons showed differences between slopes of less than 4 percent.

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE 2. COMPARISON OF UV PHOTOMETRY WITH GPT-NO

Comparison	Slope	Intercept (ppb)
1	1.010	1.8
2	1.005	3.3
3	1.036	1.3

The comparisons shown in Table 2 are of the form: (O_3 by GPT-NO) = slope x (O_3 by UV photometry) + intercept, and cover O_3 concentrations from 0 to at least 0.5 ppm. For display purposes, the data from comparison 1 is shown in Figure 4. The data covers a 19-day period and GPT-NO assays were based on two different NO cylinders during this period.

Stability of Ultraviolet Photometers Over Time--

Before the comparisons of Dasibi 1141 with the NBS photometer, Dasibi 1141 and Dasibi 1143 had been compared several times at EPA. The linear regression of these comparisons is listed as comparison 1 in Table 3. Just prior to the indirect comparison with the NBS photometer, the two Dasibis were compared (Table 3, comparison 2). Just prior to the direct comparison with the NBS photometer, the two Dasibis were again compared (Table 3, comparison 3).

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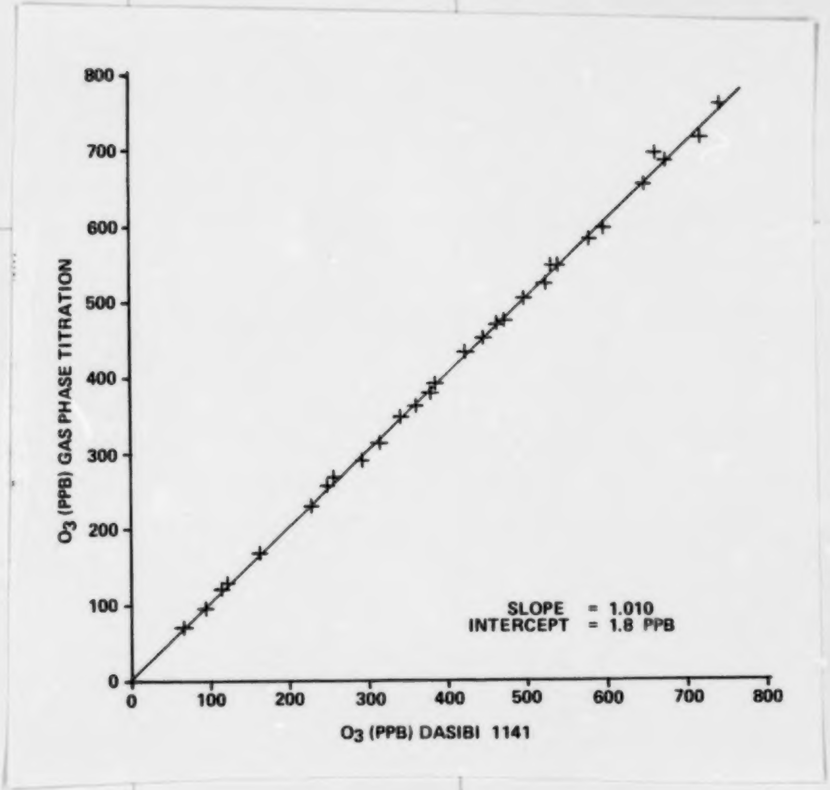

Figure 4. Comparison of Dasibi photometer with GPT-NO.

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EPA-287 (Cin.)
(4-76)

TABLE 3. COMPARISON OF DASIBI 1141 and DASIBI 1143 OVER TIME*

Comparison	Slope	Intercept (ppb)
1	0.991	0.5
2	0.982	0.7
3	0.985	-0.2

*O_3 (Dasibi 1143) = slope x O_3 (Dasibi 1141) + intercept.

Comparisons were made by generating O_3 test atmospheres and simultaneously analyzing them with both Dasibis. A linear regression was performed on the assayed concentrations. The results in Table 3 show that the difference between the two photometers was less than 2 percent for comparisons carried out over a period of at least two months, and that even transportation did not adversely affect the photometers, as comparisons 1 and 2 were made in North Carolina and comparison 3 was made in Maryland.

Summary of Conclusions from Preliminary Investigation of UV Photometric Calibration Procedure

Photometric measurements are sensitive to the quality of zero air in the sense that the same air supply must be used for both sample and reference air. However, when commercially available Dasibi O_3 analyzers are operated utilizing the described modifications, the accuracy of the instruments does not appear to be affected by modest amounts of either particles or absorbing gaseous species in the air supply.

The photometric calibration procedure agreed well with an independent method of analysis, GPT-NO, and with other photometric instruments maintained by independent laboratories, e.g., NBS.

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Photometric instruments are stable over long periods of time and may be transported without adversely affecting their reliability.

The data demonstrates that UV photometry can be used to make accurate, highly precise determinations of O_3 in calibration atmospheres. It should be noted that interference from fine particles in the air stream can cause an effect in the zero reading of the photometer but is easily recognized before any erroneous data is generated.

VARIABILITY STUDY

A study was conducted to determine the variability of the UV photometric O_3 calibration procedure. The UV photometric calibration procedure used in the study can be found in Appendix A of this report. Five volunteers (operators) of varying backgrounds participated in the study. A listing of the volunteers who participated is given in Appendix F.

Experimental

Equipment--

Volunteer UV calibration systems--Each volunteer operated one Dasibi analyzer in the field monitor configuration and one in the modified configuration (photometer). Modifications consisted of: removing the manganese dioxide converter while furnishing zero air to the instrument as reference gas; and relocating the solenoid valve and connecting it to the absorption cell using Teflon® tubing.

The second modification eliminated a zeroing problem possibly due to turbulence in the absorption cell. The magnitude of the zeroing problem ranged from a zero offset of approximately 2 to 25 ppb, depending on the manufacturing date of the instrument. Only instruments having a zero offset greater than 5 ppb were subjected to the second modification.

Reference System--The reference system consisted of three chemiluminescence O_3 analyzers, a UV photometer, an O_3 generation and dilution

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EPA-287 (Cin.)
(4-76)

system, and a dynamic AC line voltage regulator. A schematic diagram of the reference system is illustrated by Figure 5. Further description of the components within the system is given in Appendix H.

Zero Air Supply and Cleanup System--The zero air required for all test systems in the test laboratory was produced by passing house compressed air into a particle trap to remove oil and water droplets; through an MSA Ultra Filter® to remove particulates; through a Permapure Dryer® and indicating silica gel trap to remove moisture; through a pressure regulator; into an ozonator to convert any NO to NO_2; and through activated charcoal and molecular sieve to remove NO_2 and hydrocarbons (HC).

Test Ozone Generation System--A prototype National Bureau of Standards (NBS) O_3 generator was used to provide the required test atmospheres. The flow rate of zero air through the O_3 generator (10-12 l/min was controlled with a Tylan mass flow controller. Effluent from the O_3 generator was passed through a mixing chamber into a multiport sampling manifold.

Pretest Preparation--

Volunteers--Each participant was given a copy of the UV photometric O_3 calibration procedure and was asked to become familiar with it prior to his scheduled participation. Familiarization was to include actual operation of a Dasibi instrument if the participant had access to such equipment.

Test Laboratory--After initial set-up of all test laboratory systems and equipment, appropriate calibration, certification, and check-out procedures were executed to ensure that the performance of the test systems was suitable for the stated purpose of the study. These pretest operations and pertinent test data are summarized in Appendix G.

Test Procedure--

The test procedure for a given test run is as follows:

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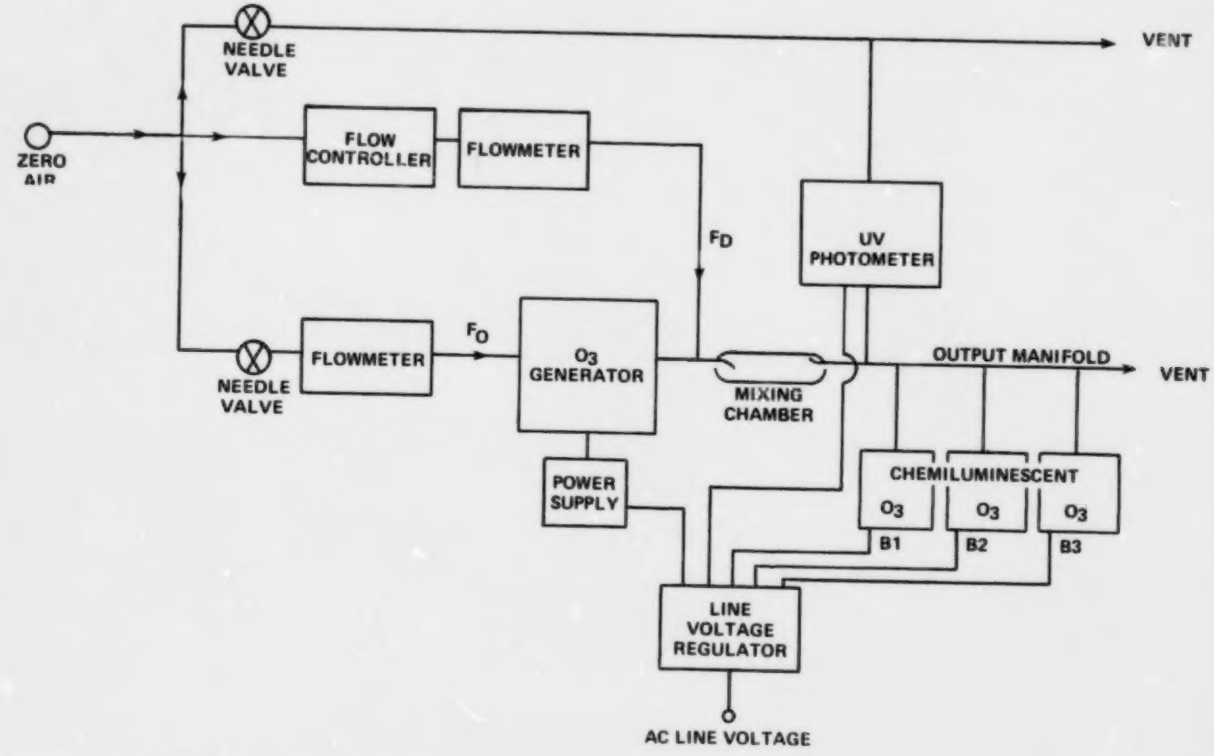
ZERO AIR
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UV PHOTOMETER
NEEDLE VALVE
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O_3 GENERATOR
MIXING CHAMBER
OUTPUT MANIFOLD
VENT
POWER SUPPLY
CHEMILUMINESCENT
O_3
O_3
O_3
B1
B2
B3
LINE VOLTAGE REGULATOR
AC LINE VOLTAGE

Figure 5. Diagram of reference system.

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- Prior to the start of the test, each volunteer prepares his Dasibi photometer and monitor according to procedures furnished by test coordinator.
- Test coordinator calibrates the three chemiluminescence analyzers with the reference system UV photometer.
- Volunteer generates O_3 test atmospheres using the test generation system. The readings from the volunteer's photometer are used for selecting the proper generator setting.
- Volunteer assays each O_3 test atmosphere with his Dasibi photometer and monitor. Simultaneous measurements are made with the chemiluminescence analyzers and reference UV photometer. Volunteer records the atmospheric pressure and absorption cell temperatures during each measurement.
- Volunteer repeats steps for O_3 generation and assay of test atmospheres.
- Volunteer submits completed data form to test coordinator.

Volunteers assayed two sets of O_3 atmospheres. Each set consisted of six O_3 concentrations (0.00, 0.40, 0.32, 0.24, 0.16, and 0.08 ppm). At the completion of the procedure, each volunteer submitted his Dasibi photometer and monitor to the test coordinator for comparison to a laboratory photometer maintained and operated by the Quality Assurance Division (QAD), EMSL, EPA/RTP.

Data Analysis and Discussion of Results

Ozone Calibrations by Ultraviolet Photometry--

For each test atmosphere, the reference system O_3 concentration was calculated as the average of the three chemiluminescence O_3 measurements.

All volunteer Dasibi readings were corrected to the temperature and pressure at the time of measurement using Equation 3-8:

$$O_3(\text{Corr}) = O_3(\text{Ind}) \times \frac{45.682}{\text{Dasibi Span No.}} \times \frac{29.92}{P} \times \frac{T}{273.15} \qquad (3\text{-}8)$$

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EPA-287 (Cin.)
(4-76)

where: O_3(Corr) = corrected O_3 concentration, ppm
O_3(Ind) = indicated O_3 concentration, ppm
45.682 = Dasibi span number at STP (0° C and 29.92 in Hg)
Dasibi Span No. = Dasibi span number during O_3 measurement
29.92 = pressure at STP, in Hg
273.15 = temperature at STP, ° K
P = ambient pressure during O_3 measurement, in Hg
T = absorption cell temperature during O_3 measurement, ° K

Least squares linear regression equations were obtained for each set of O_3 atmospheres measured in the form of Equation 1-1. Regression constants for each volunteer's Dasibi photometer and monitor are tabulated in Tables 4 and 5. The intercepts of each regression equation were not significantly different than zero.

An analysis of variance was performed on the regression slopes obtained for all UV systems and for each of the two subsets, i.e., those instruments in field monitor configuration and those modified to a photometer configuration, using the model in Equation 1-2.

The results of the analysis of variance (summarized in Table 6) for all 10 UV systems indicated a random variability (UV, $\sigma_e = 0.0033$) of about ± 0.3 percent of the mean slope. Calibration system variability was about ± 1.2 percent (UV, $\sigma_t = 0.0118$) and was statistically significant.

Each UV instrument (photometer and monitor) was referenced to a 2-meter laboratory photometer maintained and operated by QAD, EMSL, EPA/RTP. When volunteer data was corrected to the reference QAD photometer and the analysis of variance repeated on the new slopes, the second half of Table 6 ("corr") was generated. The random variability (UV "corr", $\sigma_e = 0.0033$) remained unchanged; however, the between calibration system variability (UV "corr", $\sigma_t = 0.0073$) was reduced although still statistically significant.

EPA-287 (Cin.)
(4-76)

TABLE 4. REGRESSION CONSTANTS FOR UV CALIBRATION RUNS (UV Photometer)

Volunteer	Run	Slope	σ_{Slope}	Intercept	σ_{Int}	R^2	Slope corrected to reference photometer
1	1	0.9982	0.0018	0.0004	0.0004	1.0000	1.0019
	2	0.9965	0.0015	0.0006	0.0004	1.0000	1.0002
2	1	1.0003	0.0016	0.0010	0.0004	1.0000	1.0048
	2	0.9942	0.0020	0.0010	0.0005	1.0000	0.9987
3	1	1.0082	0.0015	0.0013	0.0004	1.0000	1.0210
	2	1.0074	0.0006	0.0009	0.0002	1.0000	1.0205
4	1	0.9898	0.0017	0.0010	0.0004	1.0000	0.9996
	2	0.9897	0.0014	0.0013	0.0003	1.0000	0.9995
5	1	0.9885	0.0024	0.0002	0.0006	1.0000	0.9979
	2	0.9914	0.0010	-0.0005	0.0002	1.0000	1.0008

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EPA-287 (Cin.)
(4-76)

TABLE 5. REGRESSION CONSTANTS FOR UV CALIBRATION RUNS (UV Monitor)

Volunteer	Run	Slope	σ_{Slope}	Intercept	σ_{Int}	R^2	Slope corrected to reference photometer
1	1	1.0317	0.0049	-0.0006	0.0011	1.0000	1.0076
	2	1.0268	0.0032	-C.0003	0.0008	1.0000	1.0028
2	1	1.0057	0.0017	0.0003	0.0004	1.0000	1.0052
	2	0.9986	0.0028	0.0012	0.0007	1.0000	0.9981
3	1	1.0079	0.0030	0.0012	0.0007	1.0000	1.0210
	2	1.0017	0.0119	0.0010	0.0029	0.9997	1.0147
4	1	1.0056	0.0046	0.0022	0.0011	1.0000	1.0037
	2	0.9992	0.0020	0.0016	0.0005	1.0000	0.9973
5	1	1.0184	0.0022	-0.0009	0.0005	1.0000	1.0066
	2	1.0140	0.0017	-0.0006	0.0004	1.0000	1.0022

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE 6. VARIABILITY OF UV PHOTOMETRIC O_3 CALIBRATIONS

System	N*	Mean slope	σ_e	σ_t	σ_{tot}**	Reproducibility
UV	10	1.0037	0.0033	0.0118	0.0123	0.0341
UV monitors	5	1.0110	0.0042	0.0114	0.0121	0.0335
UV photometers	5	0.9964	0.0022	0.0072	0.0075	0.0208
UV "corr"	10	1.0052	0.0033	0.0073	0.0080	0.0222
UV monitors "corr"	5	1.0059	0.0042	0.0063	0.0076	0.0211
UV photometers "corr"	5	1.0045	0.0022	0.0091	0.0094	0.0261

*N = number of UV calibration systems

**$\sigma_{tot} = \sqrt{\sigma_e^2 + \sigma_t^2}$

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EPA-287 (Cin.)
(4-76)

Referencing to the QAD laboratory photometer had a greater effect on the monitor subset than on the photometer subset. If the Dasibi photometric instruments are operated in the field monitor configuration, the variability of field calibrations can be reduced provided the instruments are referenced to a central UV photometer (i.e., if the instruments are treated as transfer standards).

The reproducibility values in Table 6 give the maximum difference one would expect between the slopes of any two of the UV calibrations, 95 percent of the time (Equation 1-3), which works out to $\leq$ 3.5 percent of the mean slope.

The mean slopes in Table 6 show that there is no statistically significant bias of the UV systems relative to the reference system; however, it must be noted that the chemiluminescence analyzers used in the reference system were calibrated with a UV photometric system.

The analysis of variance for UV photometric O_3 calibrations is summarized in Appendix I.

Summary of Conclusions from Variability Study of Ultraviolet Photometric Calibration Procedure

Reproducibility for UV photometric calibrations using the volunteer systems was $\leq$ 3.5 percent of the mean slope. Using instruments in the photometer configuration or referencing instruments in the monitor configuration to a central UV photometer will reduce reproducibility to $\leq$ 2 percent of the mean slope.

Total variability can be broken into two parts: a random (σ_e) component and a calibration system (σ_t) component. The random component of variability for O_3 calibrations using the volunteer UV systems was about 0.3 percent of the mean slope. The calibration system component of variability for O_3 calibrations using the volunteer UV systems was about 1 percent of the mean slope. Although this variability is statistically significant and shows that the UV calibration systems can lead to biased O_3 calibrations, the magnitude of the variability these biases introduce into O_3 calibrations is less than ± 3 percent of the mean slope. The mean slope for O_3 calibrations using the volunteer UV photometric systems showed no bias with respect to the reference system, which was calibrated with a UV photometer.

Because of the low variability and good agreement between the UV photometric calibrations and the reference system, the UV photometric procedure would be a satisfactory independent calibration procedure for reference methods for the determination of O_3 concentrations in the atmosphere.

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SECTION 4

GAS PHASE TITRATION WITH EXCESS NITRIC OXIDE

INTRODUCTION

The gas phase titration with excess nitric oxide (GPT-NO) procedure is based on the reaction of O_3 with excess NO:

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (4\text{-}1)$$

When O_3 is added to excess NO in a dynamic system, the amount of NO consumed is equivalent to the amount of O_3 added and also to the amount of NO_2 produced. Using this information, an O_3 generator may be calibrated by recording both the generator settings which produce a given O_3 concentration and the corresponding change in NO concentration measured with a chemiluminescence NO analyzer. The calibrated O_3 generator may then be used to calibrate an O_3 analyzer.

PRELIMINARY INVESTIGATION

An investigation to evaluate the usefulness of the GPT-NO procedure for calibrating O_3 monitors was conducted by QAD, EMSL, EPA/RTP.

Experimental

Test Atmosphere Generation--

A schematic diagram of a GPT system typical of those used in this study is shown in Figure 6. All surfaces in contact with reactant gases and reaction products were glass, Teflon®, or other non-reactive materials.

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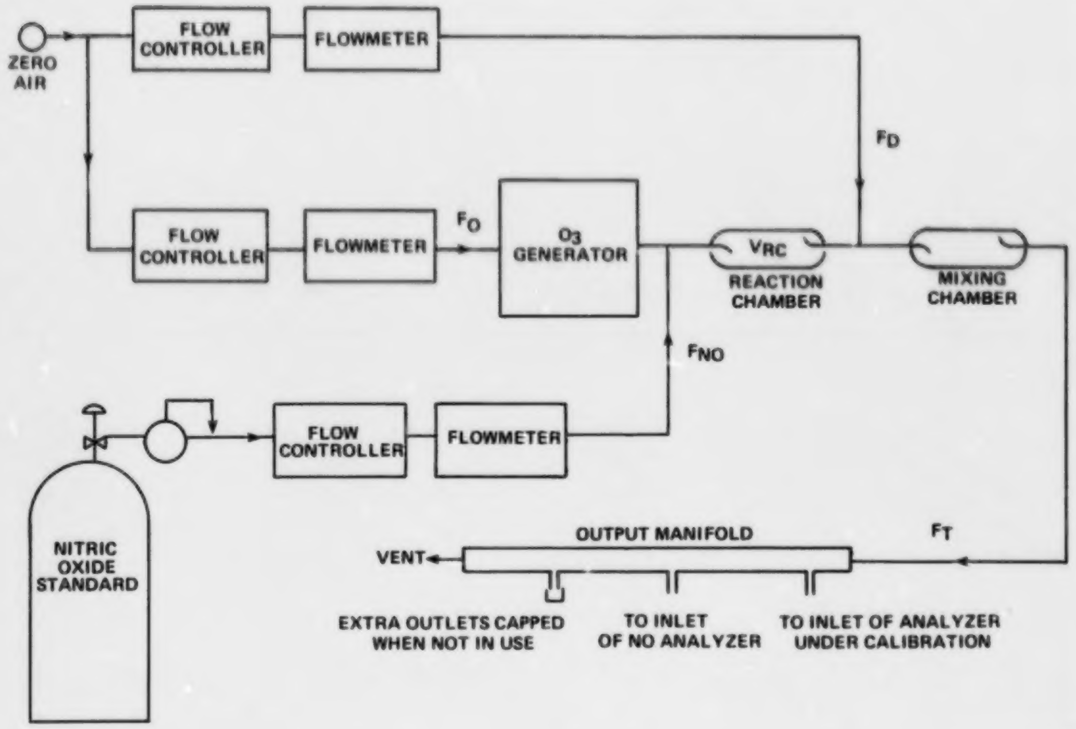
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FLOW CONTROLLER
FLOWMETER
F_D
FLOW CONTROLLER
FLOWMETER
F_O
O_3 GENERATOR
V_{RC}
REACTION CHAMBER
MIXING CHAMBER
F_{NO}
NITRIC OXIDE STANDARD
FLOW CONTROLLER
FLOWMETER
OUTPUT MANIFOLD
F_T
VENT
EXTRA OUTLETS CAPPED WHEN NOT IN USE
TO INLET OF NO ANALYZER
TO INLET OF ANALYZER UNDER CALIBRATION

Figure 6. Diagram of a typical GPT calibration system.

Ozone was continuously generated by UV irradiation of clean air passing through a quartz tube. The amount of O_3 produced was controlled by a movable sleeve surrounding the UV lamp. A constant voltage transformer was used with the UV lamp power supply to ensure stable output. The O_3 generator and its operating characteristics are described in detail by Hodgeson (9) and by the NBS (10). The generator was initially calibrated in strict accordance with the GPT-NO procedure (see Appendix B) except that a dynamic parameter specification of 2.75 was used instead of 3.75.

The apparatus used to generate NO_2 atmospheres is depicted in Figure 7. These standards were diluted with clean air gauged with a wet-test meter or soap-bubble meter. Clean air was produced by passing house air through silica gel for drying, then treating the air with O_3 to convert any NO to NO_2, and finally by scrubbing the air with a column packed with activated charcoal (6-A mesh), molecular sieve (type 4-A, 6-16 mesh), and silica gel to remove any NO_2, HC, or water.

Test Atmosphere Measurement--

Nitric oxide, NO_2, and nitrogen oxides (NO_x) measurements were made using a Bendix Model 8101-B Oxides of Nitrogen Analyzer. The analyzer was modified by incorporating a Monitor Labs "Moly Con" NO_x converter (Monitor Labs, Inc., San Diego, California). Bendix Model 8002 Chemiluminescence O_3 Monitors were used as O_3 analyzers. Comparative UV O_3 measurements were made with Dasibi Model 1003-AH O_3 Analyzers. The Dasibi analyzers were modified by replacing the analyzer's O_3 converter with a sample line connected to a zero air source.

Reagents--

Nitric oxide was obtained from NBS-Standard Reference Material (SRM) No. 1683, 50 ppm NO in nitrogen. Nitrogen dioxide was obtained from a gravimetrically calibrated NO_2 permeation device similar to NBS-SRM No. 1629. The permeation device was weighed periodically throughout the study to ensure an accurate value for the permeation rate.

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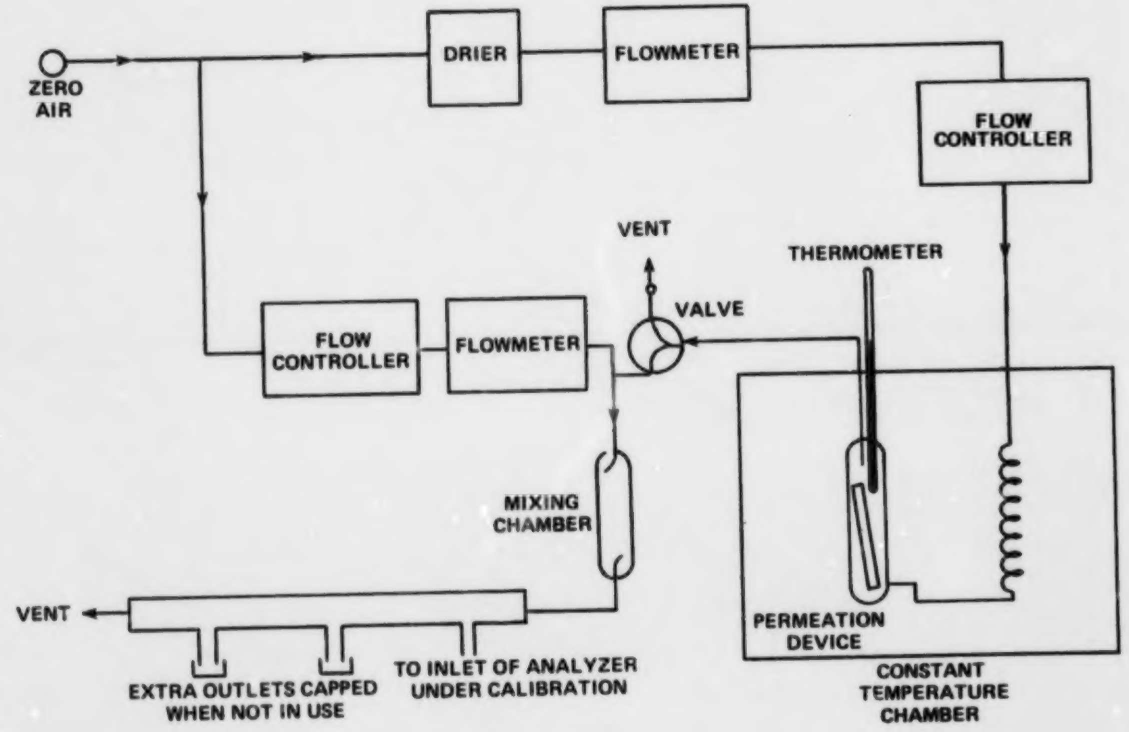
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PERMEATION DEVICE
CONSTANT TEMPERATURE CHAMBER
VENT
EXTRA OUTLETS CAPPED WHEN NOT IN USE
TO INLET OF ANALYZER UNDER CALIBRATION

Figure 7. Diagram of calibration apparatus using NO_2 permeation device.

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Results and Discussion

Verification of Dynamic Parameter Specification--

In order for GPT-NO to be a valid means of calibration for O_3 sources, the reaction of O_3 with excess NO must be quantitative (i.e., all of the O_3 must react). The following dynamic parameter specification:

$$P_R = [NO]_{RC} \times t_R \geq 3.75 \text{ ppm-min} \qquad (4\text{-}2)$$

where: P_R = dynamic parameter, ppm-min
$[NO]_{RC}$ = NO concentration in the reaction chamber, ppm
t_R = residence time in the reaction chamber, min

assures that the reaction of O_3 is quantitative ($\geq$ 99 percent) when up to 90 percent of the initial NO is consumed. The 3.75 ppm-min factor is based on empirical measurements by Rehme and Smith (unpublished data) and includes a safety factor to ensure quantitative reaction.

The validity of the specification was verified by substituting various values for P_R and measuring the residual O_3 during a GPT. The completeness of reaction, defined as:

$$\frac{\Delta NO}{\Delta NO + O_{3\text{ Residual}}}$$

was determined in the region of 90 percent NO consumed at various dynamic parameter values for several sizes of reaction chambers and total flowrates. The data is shown graphically in Figures 8, 9, and 10. Total flows of 1.5, 5.0, and 10.0 l/min with reaction chamber volumes of 0.100, 0.200, and 0.500 l, respectively, were used. The data show that at 1.5 and 5.0 l/min and with 90 percent of the NO consumed, the reaction is more than 99 percent complete for dynamic parameter values of 2.0 or greater. However, at a flow of 10.0 l/min, the reaction was approximately 98.6 percent complete using a factor of 3.0. Changing the reaction chamber volume to 0.700 l to

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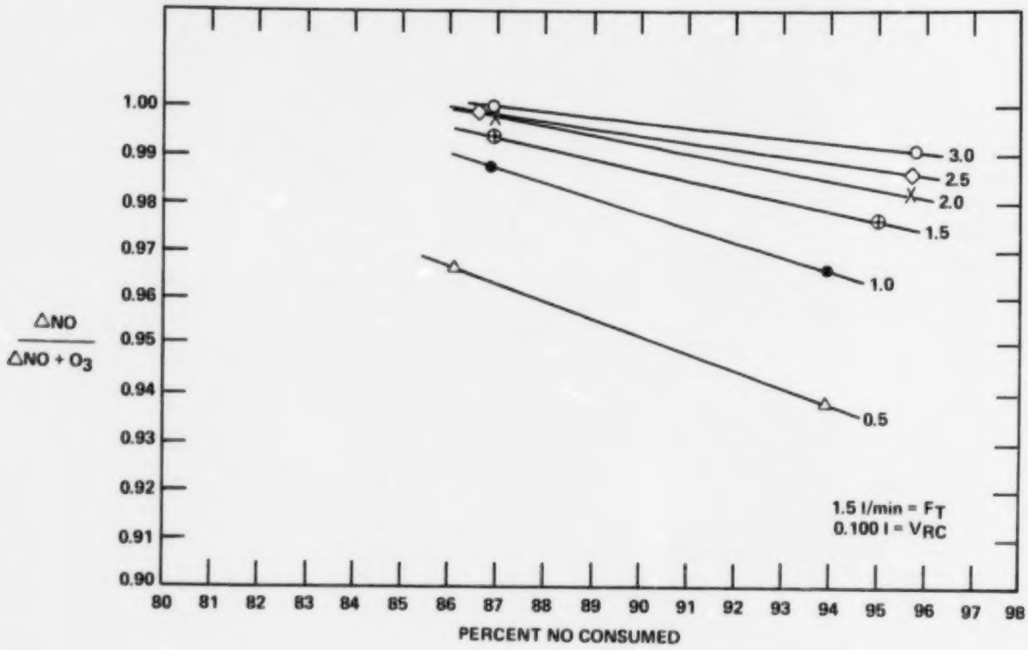

Figure 8. Completeness of reaction versus NO consumed at various dynamic parameter specifications.

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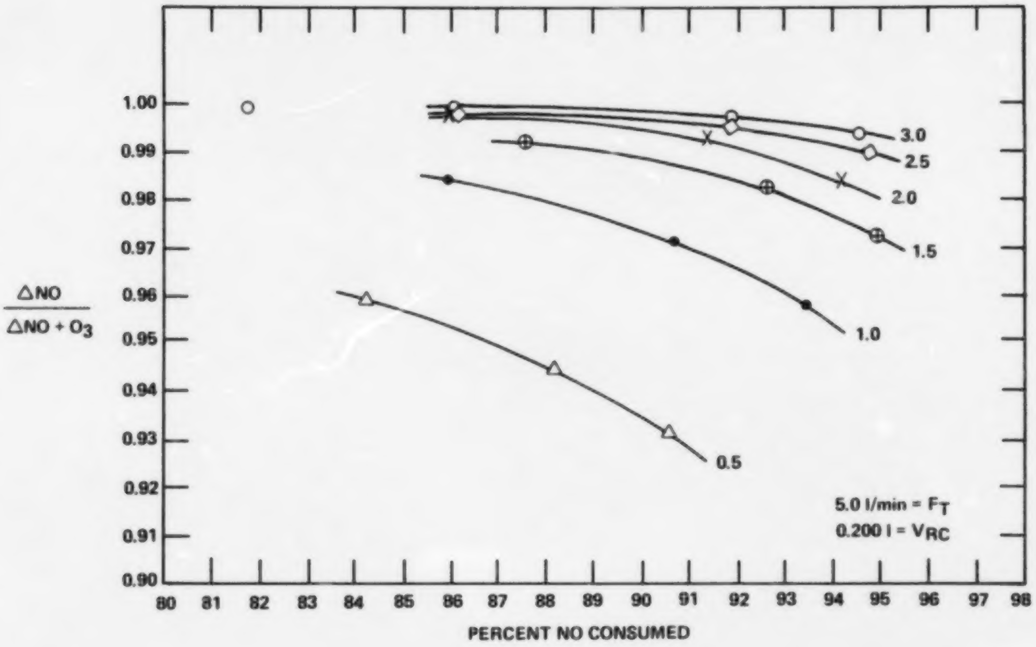

Figure 9. Completeness of reaction versus NO consumed at various dynamic parameter specifications.

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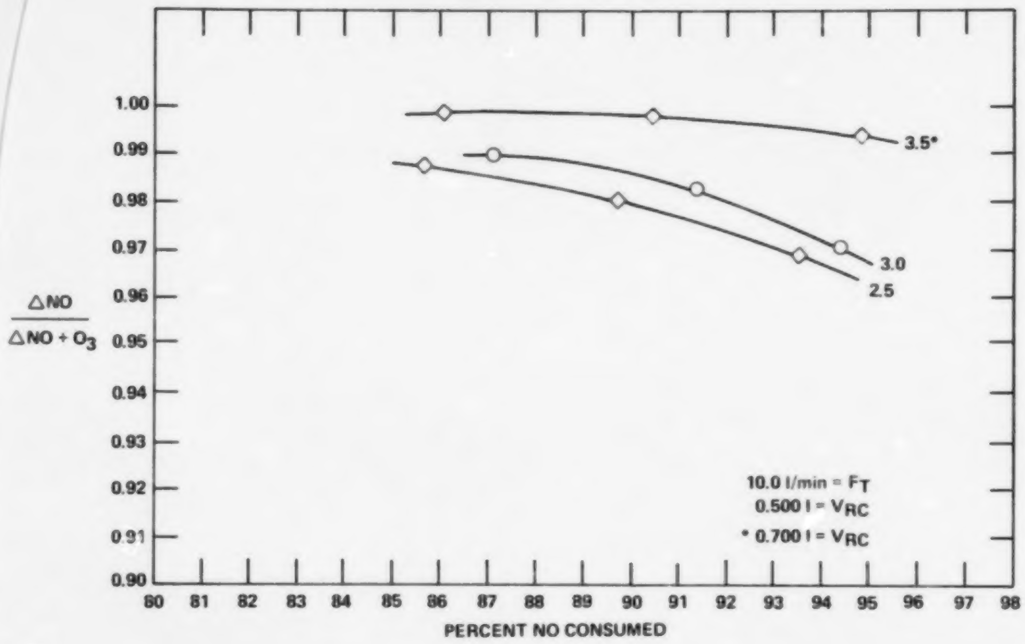

Figure 10. Completeness of reaction versus NO consumed at various dynamic parameter specifications.

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produce a dynamic parameter of 3.5, yielded a 99.8 percent complete reaction at 90 percent NO consumed.

Comparison of Gas Phase Titration with Excess Nitric Oxide Ozone Calibration Options--

The GPT-NO procedure describes three means for relating the response of an O_3 analyzer to a GPT calibrated O_3 source. In the primary procedure, the O_3 generator settings are recorded with their corresponding NO concentration changes (ΔNO) during GPT. The O_3 equivalent to the ΔNO is calculated for each generator setting and the NO source is removed from the GPT system. The generator settings are then repeated to produce the O_3 concentration standards.

In Option 1, a single O_3 concentration is generated and assayed by GPT and then diluted to appropriate calibration levels. Option 1 was tested at two flow levels. In the first test, the O_3 source was operated at an initial total flow of 5.5 l/min, with a GPT assayed O_3 concentration of 0.525 ppm. Several lower O_3 concentrations were obtained by dilution. An additional lower O_3 concentration was generated and assayed by GPT and approriate dilutions were made to produce the lower calibration points. The data for this comparison is given in Table 7. The table shows the O_3 measured by a chemiluminescence O_3 monitor, the total air flow, the dilution ratio, the amount of dilution air, the predicted O_3 (calculated from flow dilution), and the ratio of the measured O_3 to the predicted O_3. The data show the measured O_3 concentrations to be within 2 to 3 percent of the predicted values.

A second test was performed starting with an O_3 concentration of 0.500 ppm and an initial total flow of 1.3 l/min. Data for this test is given in Table 8. Again, the measured to predicted O_3 ratios are in good agreement.

Option 2 is basically the same as the primary procedure. However, the NO source is diverted from the GPT system after each O_3 concentration

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TABLE 7. GPT-NO O_3 ANALYZER CALIBRATION USING OPTION 1 (Test No.1)*

$[O_3]_{Mon}$	$F_O + F_D + F_{D'}$	$\frac{F_O + F_D}{F_O + F_D + F_{D'}}$	$F_{D'}$	$[O_3]_{Pred}$	$\frac{[O_3]_{Mon}}{[O_3]_{Pred}}$
0.525†	5.542	1.000	0.000	0.525	1.000
0.397	7.436	0.745	1.894	0.391	1.024
0.340	8.766	0.632	3.224	0.332	1.024
0.308	9.582	0.578	4.040	0.303	1.015
0.237	12.500	0.443	6.958	0.232	1.018
0.216	13.654	0.406	8.112	0.213	1.014
		Mean ± S.D. = 1.019 ± 0.005			
0.240‡	5.542	1.000	0.000	0.240	1.000
0.200	6.448	0.859	0.906	0.206	0.970
0.165	7.845	0.706	2.303	0.170	0.973
0.095	13.654	0.406	8.112	0.097	0.979
		Mean ± S.D. = 0.974 ± 0.005			
		Overall Mean = 1.002 ± 0.023			

*F_T = initial total flow 5.5 l/min

$[O_3]_{Mon}$ = measured O_3 concentration, ppm

$F_O + F_D + F_{D'}$ = total air flow, l/min

$\frac{F_O + F_D}{F_O + F_D + F_{D'}}$ = dilution ratio

$F_{D'}$ = dilution air flow, l/min

$[O_3]_{Pred}$ = predicted O_3 concentration, ppm

$\frac{[O_3]_{Mon}}{[O_3]_{Pred}}$ = ratio of the measured to the predicted O_3 concentration

†GPT assayed O_3 concentration at generator sleeve setting of 6

‡GPT assayed O_3 concentration at generator sleeve setting of 3

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TABLE 8. GPT-NO O_3 ANALYZER CALIBRATION USING OPTION 1 (Test No. 2)*

$[O_3]_{Mon}$	$F_O + F_D + F_{D'}$	$\frac{F_O + F_D}{F_O + F_D + F_{D'}}$	$F_{D'}$	$[O_3]_{Pred}$	$\frac{[O_3]_{Mon}}{[O_3]_{Pred}}$
0.500†	1.290	1.000	0.000	0.500	1.000
0.292	2.200	0.586	0.910	0.293	0.996
0.202	3.178	0.406	1.889	0.203	0.996
0.102	6.269	0.206	4.979	0.103	0.991
0.065	9.551	0.135	8.261	0.068	0.963
		Mean ± S.D. = 0.986 ± 0.016			

*F_T = initial total flow 1.3 l/min

$[O_3]_{Mon}$ = measured O_3 concentration, ppm

$F_O + F_D + F_{D'}$ = total air flow, l/min

$\frac{F_O + F_D}{F_O + F_D + F_{D'}}$ = dilution ratio

$F_{D'}$ = dilution air flow, l/min

$[O_3]_{Pred}$ = predicted O_3 concentration, ppm

$\frac{[O_3]_{Mon}}{[O_3]_{Pred}}$ = ratio of the measured to the predicted O_3 concentrations

†GPT assayed O_3 concentration at generator sleeve setting of 1.7

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EPA-287 (Cin.)
(4-76)

is assayed. Thus, O_3 concentrations are supplied to the O_3 analyzer under calibration intermittently during the titration rather than at its completion. Option 2 was tested by performing a GPT calibration of an O_3 monitor, interrupting the NO flow as required. At the completion of the GPT, these same O_3 concentrations were supplied to the monitor (by repeating the O_3 generator settings) as would be done in the primary procedure. Data for this comparison are given in Table 9 and show that the two calibration techniques are in good agreement.

TABLE 9. GPT-NO O_3 ANALYZER CALIBRATION USING OPTION 2

$[O_3]_{GPT}$, ppm	Analyzer response, % chart (Option 2)*	Analyzer response, % chart (Primary Procedure)†
0.487	97.4	98.0
0.352	70.6	71.4
0.218	44.4	44.6
0.098	19.0	19.8
0.000	0.8	0.8

*Analyzer response (Option 2) = 199.4 $[O_3]_{GPT}$ + 0.4

†Analyzer response (Primary Procedure) = 200.3 $[O_3]_{GPT}$ + 0.6

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Comparison of Ozone Measurements by Gas Phase Titration with Excess Nitric Oxide and Ultraviolet Photometry--

Ozone concentrations generated and assayed by GPT-NO were measured by UV photometry using two modified Dasibi O_3 analyzers. The results of these comparisons are given in Table 10. The O_3 concentrations measured by GPT-NO were approximately 8 percent higher than measurements by UV photometry. Several previous investigators reported a one-to-one agreement between GPT-NO and UV O_3 measurements (6, 11, 12). Reasons for the dis-

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EPA-287 (Cin.)
(4-76)

agreement between our comparisons and those reported in the literature were not readily apparent. Both the GPT system and the UV photometers were checked for O_3 losses or other problems that might account for this discrepancy but specific reasons remained obscure.

TABLE 10. COMPARISON OF $[O_3]_{GPT\text{-}NO}:[O_3]_{UV}$ RATIOS

Date	Dasibi No. 1*	Dasibi No. 2†
9/29/76	1.096	-
9/30/76	1.094	-
10/01/76	1.068	-
10/12/76	1.085	1.088
10/15/76	1.077	1.076
10/20/76	1.074	1.074
Mean	1.082	1.079
S.D.	0.011	0.008

*Dasibi No. 1, S/N 1673

†Dasibi No. 2, S/N 1052

Comparison of Nitrogen Dioxide Generated by Gas Phase Titration with Excess Nitric Oxide and Permeation Devices--

The GPT-NO calibration procedure was checked for internal consistency by measuring the NO_2 produced during GPT on the NO_2 channel of an $NO\text{-}NO_x\text{-}NO_2$ analyzer calibrated with an NBS-SRM NO_2 permeation device. A departure from the expected one-to-one ratio is evidence of some systematic error or incorrect calibration of the permeation device. Table 11 lists these comparisons for ten GPT calibrations done on ten different days. Agreement between the NO_2 produced by the NBS-SRM NO_2 permeation device and the NO_2 produced by GPT was within ± 2 percent.

EPA-287 (Cin.)
(4-76)

TABLE 11. COMPARISON OF $[NO_2]_{PD}$ VERSUS $[NO_2]_{GPT}$*

Calibration	$\frac{[NO_2]_{PD}}{[NO_2]_{GPT}}$
1	1.002
2	1.002
3	0.986
4	1.002
5	1.010
6	1.018
7	0.990
8	0.991
9	0.996
10	1.005

* Mean $\frac{[NO_2]_{PD}}{[NO_2]_{GPT}}$ ± 1 S.D. = 1.000 ± 0.010

Stability of Output of Ozone Generator Calibrated by Gas Phase Titration with Excess Nitric Oxide--

Table 12 gives the outputs of an O_3 generator at two sleeve settings over a period of about 30 days. Variability of generator outputs due to day-to-day variations in flowrate was eliminated by normalizing the outputs to a standard flowrate of 5.0 l/min. Variability over 30 days at each generator setting was less than 3 percent.

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EPA-287 (Cin.)
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TABLE 12. O_3 GENERATOR OUTPUT STABILITY

Day	Date	S.S. = 30	S.S. = 50
1	09/29/76	0.245	0.444
2	09/30/76	0.242	0.441
3	10/01/76	0.246	0.450
14	10/12/76	0.265	-
17	10/15/76	0.250	-
22	10/20/76	0.249	0.453
23	10/21/76	0.254	0.460
28	10/26/76	0.245	0.446
30	10/28/76	0.258	0.468
n		9	7
Mean		0.250	0.452
S.D.		0.007	0.010
%		2.9	2.1

Summary of Conclusions from Preliminary Investigation of Gas Phase Titration with Excess Nitric Oxide Calibration Procedure

The GPT-NO O_3 calibration procedure is capable of producing a calibrated O_3 source which can be used to calibrate an O_3 analyzer. While the day-to-day repeatability of a GPT-NO system is very good, the accuracy of the procedure may be questionable.

Calibration Options 1 and 2 (dilution and NO interruption during GPT) produced calibrations in good agreement with the primary method described by the procedure.

A dynamic parameter specification of 3.75 was more than adequate to ensure a quantitative reaction at total flows of 1.5, 5.0, and 10.0 l/min and reaction chamber volumes of 0.100, 0.200, and 0.700 l. A specification

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of 2.00 is capable of producing a 99+ percent complete reaction at the 1.5 and 5.0 l/min flows and is probably adequate for the 10.0 l/min flow.

The ultimate utility of GPT-NO as an independent calibration procedure cannot be determined until the discrepancy between $[O_3]_{GPT}$ and $[O_3]_{UV}$ has been resolved. The GPT data confirms that for every NO molecule consumed, an NO_2 molecule is generated.

VARIABILITY STUDY

A study was conducted to determine the variability of the GPT-NO O_3 calibration procedure. The GPT-NO calibration procedure used in the study can be found in Appendix B of this report. Ten operators with varying degrees of experience were selected for participation in the variability study. The volunteers ranged from technicians experienced in routine calibration of air monitoring instrumentation to professionals experienced in the development and application of air monitoring techniques and associated calibration procedures.

Experimental

Equipment--

Volunteer Gas Phase Titration Systems--The volunteers were instructed to furnish a GPT calibration system for the study. Specific equipment (commercial, modified commercial, and operator-assembled) was recommended in some cases in order to include a mixture of the available GPT apparatus in the study. Each GPT system consisted of four main components: the air supply and cleanup system, the NO standard, the NO-O_3 reaction and dilution system, and the flow measurement equipment. The test protocol required that the GPT system provide a total flow of at least 4.0 l/min. The volunteers were not required to furnish the chemiluminescence NO analyzer necessary for the procedure.

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A listing of the volunteers who participated in the study and a description of their GPT calibration systems appears in Appendix F.

Reference System--The reference system consisted of three chemiluminescence O_3 analyzers, a UV photometer, an O_3 generation and dilution system, and a dynamic AC line voltage regulator (see Figure 5). A description of the components within the system is given in Appendix H.

Control System--The control system was a laboratory assembled GPT calibration apparatus with associated equipment (see Figure 11). For a complete description of the components within the system see Appendix H.

Zero Air Supply and Cleanup System--The zero air required for all test systems in the test laboratory was produced by first passing house compressed air into a particle trap to remove oil and water droplets, and then through an MSA Ultra Filter® to remove particulates. The air was then passed through a Permapure Dryer® and indicating silica gel trap to remove moisture, through a pressure regulator, into an ozonator to convert any NO to NO_2, and finally through activated charcoal and molecular sieve to remove NO_2 and HC.

Nitrogen Dioxide Permeation System--The NO_2 permeation system is shown schematically in Figure 12. A description of the components within the system is given in Appendix H.

Reference Flow Measurement Equipment--Reference flow measurements were obtained using a Precision Scientific 3.0 l/revolution wet-test meter (certified against a spirometer and an NBS traceable bubble flowmeter) for zero air flows and a Hastings Miniflow Kit certified (NBS traceable) 10-cm^3 bubble flowmeter for NO flows.

Nitric Oxide Standard Cylinder Analysis System--The assay of volunteer NO standards was performed using a Bendix Model 8101-C $NO\text{-}NO_2\text{-}NO_x$ Analyzer operated on the 0 to 100 ppm range. The NO concentration of each standard was measured by direct comparison (without dilution) to two NBS-SRM's (No. 1683 and No. 1684).

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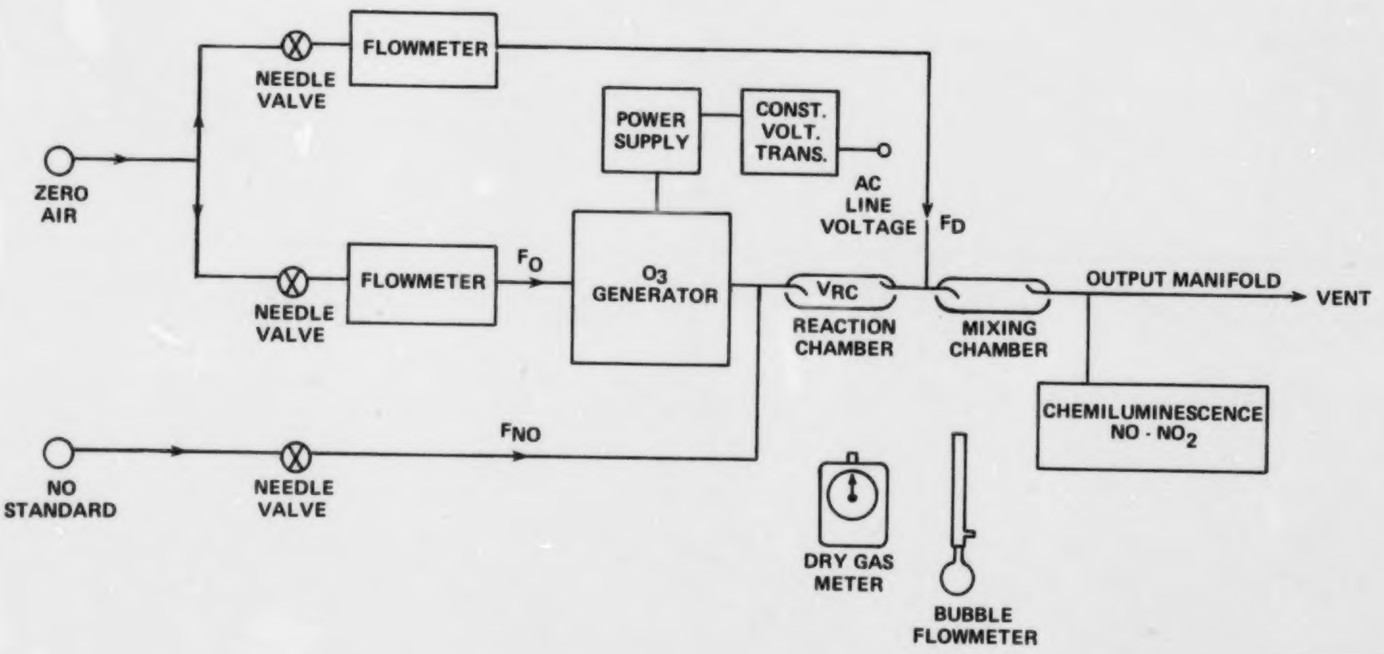
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O_3 GENERATOR
F_D
V_{RC}
REACTION CHAMBER
MIXING CHAMBER
OUTPUT MANIFOLD
VENT
CHEMILUMINESCENCE NO · NO_2
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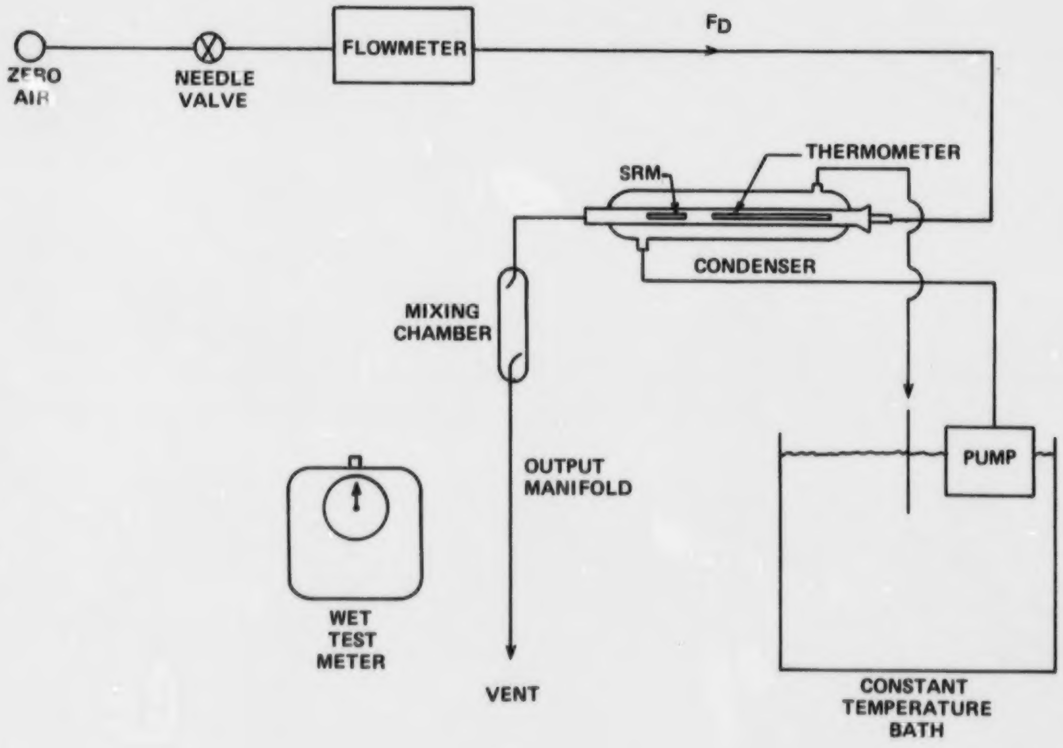
NEEDLE VALVE
F_{NO}
DRY GAS METER
BUBBLE FLOWMETER

Figure 11. Diagram of control GPT system.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SRM
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PUMP
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VENT
CONSTANT TEMPERATURE BATH

Figure 12. Diagram of NO_2 permeation system.

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Pretest Preparation--

Volunteers--Each volunteer was given a copy of the GPT-NO O_3 calibration procedure and instructed to verify that his GPT calibration system met the specifications given in the calibration procedure. Volunteers were encouraged to become familiar with the procedure by performing practice calibrations and applicable check-out procedures prior to participating in the study.

Test Laboratory--Following the initial set-up of all test laboratory systems and equipment, appropriate calibration, certification, and check-out procedures were carried out to ensure that the performance of the test systems was suitable for the stated purpose of the study. These pretest operations and pertinent test data are summarized in Appendix G.

Test Procedure--

The study was designed so that two volunteers could participate simultaneously on any given test day, one using his own GPT system and the other using the control GPT system. Volunteers were briefed on the test procedures and operation of the control GPT system. Volunteers were allowed sufficient time for equipment set-up and any preliminary check-out operations. The test procedure for a given test run is given below:

- Test coordinator calibrates the three chemiluminescence O_3 analyzers in the reference system against the UV photometer.
- Test coordinator obtains reference flow measurements (zero air and standard NO flows) immediately after volunteer makes the flow measurements. (This step applies only to volunteer GPT systems.).
- Volunteer calibrates the O_3 generator within the GPT system using the GPT-NO calibration procedure and prepares an O_3 generator calibration curve.
- Test coordinator measures the NO_2 produced during each GPT step using a chemiluminescence NO_x analyzer. Test coordinator performs 2-point NO_2 calibration (zero and span) of this analyzer immediately before or after the measurements using the NO_2 permeation system.

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- Volunteer generates six levels of O_3 (0.00, 0.40, 0.32, 0.24, 0.16, 0.08 ppm) which are measured with the O_3 analyzers in the reference system.

- Volunteer submits completed data form and O_3 generator calibration curve to test coordinator.

Each volunteer generated two sets of O_3 atmospheres using his own GPT system and two sets of O_3 atmospheres using the control GPT system. The number of test days required for a given volunteer to complete the tests varied from 2 to 4 days. Upon completion, each volunteer submitted his NO standard (cylinder) to the test coordinator for analysis. The NO assay procedure is given in Appendix H.

Data Analysis and Discussion of Results

Ozone Calibrations by Gas Phase Titration with Excess Nitric Oxide--

For each O_3 concentration generated, the reference system O_3 concentration was calculated as the average of the three chemiluminescence O_3 measurements. A least squares linear regression equation was obtained for each set of O_3 atmospheres that was generated. Each regression equation was in the form of Equation 1-1. The regression constants for the control and volunteer GPT systems are given in Tables 13 and 14, respectively. The intercepts (B_2) of all the regression equations were examined statistically: they were not significantly different than zero.

An analysis of variance was performed on the regression slopes from both the volunteer and control systems using the model of Equation 1-2. In this simple analysis of variance, each cell for a given GPT system (volunteer or control) contains the two replicate slopes obtained for each volunteer; thus, B_{11} and B_{12} are regression slopes obtained by volunteer number one for runs 1 and 2, respectively.

Variability data derived from regression slope values obtained on the control system are given in Table 15 (Control). The random component of the variability (σ_e = 0.0212) was approximately ± 2 percent of the mean slope;

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TABLE 13. REGRESSION CONSTANTS FOR GPT-NO CONTROL SYSTEM CALIBRATION RUNS

Volunteer	Run	Slope	σ_{Slope}	Intercept	σ_{Int}	R^2
1	1	1.0532	0.0068	-0.0012	0.0016	0.9998
	2	1.0221	0.0083	0.0005	0.0020	0.9997
2	1	1.0585	0.0045	-0.0019	0.0010	0.9999
	2	1.0200	0.0065	-0.0010	0.0016	0.9998
3	1	1.0148	0.0064	0.0013	0.0015	0.9998
	2	1.0280	0.0052	0.0012	0.0012	0.9999
4	1	1.0183	0.0062	-0.0013	0.0015	0.9999
	2	1.0540	0.0088	0.0012	0.0020	0.9997
5	1	1.0003	0.0075	0.0006	0.0019	0.9998
	2	1.0602	0.0116	-0.0011	0.0029	0.9995
6	1	1.0612	0.0065	0.0019	0.0015	0.9999
	2	1.0276	0.0081	-0.0020	0.0019	0.9997
7	1	1.0289	0.0034	0.0005	0.0008	1.0000
	2	1.0407	0.0069	-0.0013	0.0016	0.9998
8	1	1.0274	0.0089	0.0028	0.0021	0.9997
	2	1.0323	0.0087	0.0021	0.0020	0.9997
9	1	1.0299	0.0051	0.0004	0.0012	0.9999
	2	1.0207	0.0060	-0.0009	0.0014	0.9999
10	1	1.0100	0.0085	0.0039	0.0020	0.9997
	2	1.0222	0.0066	0.0001	0.0016	0.9998

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE 14. REGRESSION CONSTANTS FOR GPT-NO VOLUNTEER SYSTEM CALIBRATION RUNS

Volunteer	Run	Slope	σ_{Slope}	Intercept	σ_{Int}	R^2	Type
1	1	1.0953	0.0147	-0.0019	0.0033	0.9993	Bendix Table
	2	1.1083	0.0067	0.0028	0.0015	0.9999	
2	1	1.0410	0.0066	-0.0024	0.0015	0.9998	Teco
	2	1.0401	0.0036	-0.0002	0.0008	1.0000	
3	1	1.1212	0.0094	0.0027	0.0020	0.9997	Bendix Suitcase
	2	1.0828	0.0150	0.0017	0.0033	0.9992	
4	1	1.0918	0.0106	0.0027	0.0023	0.9996	Operator Assembled
	2	1.0654	0.0051	-0.0022	0.0012	0.9999	
5	1	1.1192	0.0111	-0.0016	0.0024	0.9996	Bendix Suitcase
	2	1.1532	0.0210	-0.0069	0.0045	0.9987	
6	1	1.0340	0.0220	0.0083	0.0050	0.9982	Bendix Suitcase
	2	1.0764	0.0212	-0.0050	0.0053	0.9988	
7	1	1.1200	0.0063	0.0022	0.0014	0.9999	Operator Assembled
	2	1.0864	0.0066	0.0019	0.0015	0.9999	
8	1	1.0339	0.0278	0.0057	0.0064	0.9971	Operator Assembled
	2	1.0594	0.0285	0.0016	0.0065	0.9971	
9	1	1.0490	0.0070	0.0033	0.0016	0.9998	Operator Assembled
	2	1.0489	0.0051	0.0002	0.0012	0.9999	
10	1	1.0520	0.0055	0.0031	0.0012	0.9999	Bendix Table
	2	1.0071	0.0141	0.0051	0.0033	0.9992	

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EPA-287 (Cin.)
(4-78)

the calibration system component of the variability ($\sigma_t = 0$) was negligible. Since the differences in the calibration systems for the control GPT calibration system are only the ten operators, the analysis of variance results indicate that the operators do not make an identifiable contribution to the total variability other than in the random effects. Total variability for O_3 calibrations performed with the control system is comprised solely of the random component of variability.

TABLE 15. VARIABILITY OF GPT-NO O_3 CALIBRATIONS

System	N*	Mean Slope	σ_e	σ_t	σ_{tot}**	Reproducibility
Control	10	1.0315	0.0212	0.0000	0.0212	0.0588
Volunteer	10	1.0742	0.0213	0.0318	0.0383	0.1062
Corrected Volunteer	10	1.0576	0.0196	0.0231	0.0303	0.0840

*N = number of participating volunteers

**$\sigma_{tot} = \sqrt{\sigma_e^2 + \sigma_t^2}$

The random component of variability ($\sigma_e = 0.0213$) for O_3 calibrations performed with the volunteer systems (Table 15, Volunteer) was the same as for the control system, i.e., about ± 2 percent of the mean slope. The calibration system component of variability ($\sigma_t = 0.0318$), however, was significant and amounted to approximately ± 3 percent of the mean slope. Assuming that the results from the control system are applicable to the volunteer systems, and the operators' contribution to the total variability is in the random component, then the significant calibration system variability represents the different volunteer GPT calibration equipment.

Reference flow measurements were obtained during each calibration performed with the volunteer systems. The NO standards (cylinders) supplied by the volunteers as part of their GPT systems were assayed against two independent NO standards. From these reference measurements, the O_3 (Volunteer) values and regression equations (Equation 1-1) were recalculated. The corrected slopes for the volunteer GPT systems are given in Table 16.

TABLE 16. GPT-NO SUPPLEMENTAL MEASUREMENTS AND CORRECTED O_3 CALIBRATION SLOPES FOR VOLUNTEER SYSTEMS

Volunteer	Run	NO (Vol) / NO (Ref)	NO Flow (Vol) / NO Flow (Ref)	Dil Flow (Vol) / Dil Flow (Ref)	Correction Factor	Corrected Slope
1	1	1.0073	1.0134	0.9990	0.9787	1.0720
	2		1.0252	1.0185	0.9863	1.0931
2	1	0.9993	0.9707	1.0012	1.0321	1.0744
	2		0.9836	1.0007	1.0181	1.0589
3	1	1.0416	0.9971	0.9879	0.9512	1.0665
	2		0.9945	0.9802	0.9463	1.0247
4	1	0.9950	1.0122	0.9855	0.9785	1.0683
	2		1.0008	0.9818	0.9859	1.0504
5	1	1.0002	1.0096	0.9956	0.9859	1.1034
	2		1.0029	0.9793	0.9763	1.1259
6	1	0.9930	1.0025	0.9901	0.9946	1.0284
	2		1.0041	0.9890	0.9919	1.0677
7	1	1.0089	1.0248	0.9809	0.9487	1.0625
	2		1.0010	0.9780	0.9684	1.0521
8	1	1.0006	0.9932	0.9767	0.9828	1.0161
	2		1.0150	0.9722	0.9572	1.0141
9	1	0.9796	1.0084	0.9920	1.0042	1.0534
	2		1.0127	0.9903	0.9982	1.0470
10	1	0.9880	0.9913	0.9890	1.0098	1.0623
	2		1.0013	0.9925	1.0032	1.0103

An analysis of variance was performed on the corrected slopes and the results are given in Table 15 (Corrected Volunteer). The random component of variability ($\sigma_e = 0.0196$) was again ± 2 percent of the mean slope; the calibration system component of variability ($\sigma_t = 0.0231$) was still significant and amounted to about ± 2 percent of the mean slope. While corrections for flow measurements and cylinder assay slightly reduce the overall variability, the equipment used for GPT-NO O_3 calibrations will still contribute to the overall variability.

Results from the control system show that reproducibility (Equation 1-3) will be within 6 percent, 95 percent of the time. Results from the volunteer systems show that reproducibility will be within 10.5 percent, 95 percent of the time. When all flow measurements and NO cylinder assays are referenced to a central laboratory, reproducibility can be reduced to about 8.5 percent as seen in the corrected volunteer results.

Mean slopes for both control and volunteer GPT systems show a positive bias with respect to the UV calibrated reference system. The control system results yielded an average bias of + 3 percent (mean slope = 1.0315), while the average bias obtained with volunteer systems was + 7.5 percent (mean slope = 1.0742). These results indicate that the GPT calibration systems in use today contribute a positive bias to O_3 calibrations.

The analysis of variance for GPT-NO O_3 calibrations is summarized in Appendix I.

Nitrogen Dioxide Calibrations by Gas Phase Titration with Excess Nitric Oxide--

During the volunteer O_3 calibrations, an NO_2 reference system calibrated with an NBS-SRM NO_2 permeation tube measured the NO_2 generated during each intermediate step of the GPT procedure. The measured NO_2 concentrations were then compared to the corresponding changes in NO concentration (ΔNO). A least squares linear regression was obtained for each set of NO_2 concentrations generated:

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(4-76)

$$\Delta\text{NO (from GPT step)} = C_1\ \text{NO}_2\ \text{(Reference)} + C_2 \qquad (4\text{-}3)$$

The regression slopes for the volunteer and control GPT systems are given in Table 17. Again, intercepts (C_2) of all these regression equations were not significantly different than zero. An analysis of variance was then performed on these regression slopes using the same model as for O_3 calibrations by GPT-NO. The results of the analysis of variance of the regression slopes are given in Table 18.

The random variability ($\sigma_e = 0.0158$) for NO_2 calibrations performed using the control system was about ± 1.5 percent of the mean slope. The calibration system variability ($\sigma_t = 0.0075$) was not statistically significant. Again, this result was interpreted to mean that there are no operator contributions to the total variability, excluding random effects.

The random variability ($\sigma_e = 0.0150$) for NO_2 calibrations performed using volunteer systems (Table 18, Volunteer) was similar to the control system (± 1.5 percent of the mean slope). The calibration system variability ($\sigma_t = 0.0219$) was significant and amounted to about ± 2 percent of the mean slope. Once more, the GPT calibration equipment makes a significant contribution to the total variability.

If ΔNO values are corrected for reference flow measurements and NO cylinder assays as were preceding O_3 generated values, a corrected set of regression equations can be generated for the volunteer system (see Table 17). An analysis of variance was performed on the corrected slopes and the results are given in Table 18 (Corrected Volunteer). Random variability ($\sigma_e = 0.0140$) was ± 1.5 percent of the mean slope; calibration system variability ($\sigma_t = 0.0059$) was statistically insignificant. If the flow measurements and cylinder assays are referenced to a central laboratory for GPT-NO NO_2 calibrations, the overall variability can be reduced to the random variability level.

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(4-76)

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TABLE 17. REGRESSION SLOPES FOR CHANGE IN NO (Volunteer GPT) VERSUS NO_2 (Reference Measurement)

Volunteer	Run	Slope $\Delta NO/NO_2$ Control System	Slope $\Delta NO/NO_2$ Volunteer System	Slope $\Delta NO/NO_2$* Volunteer System
1	1	0.9981	1.0384	1.0012
	2	1.0182	1.0224	0.9934
2	1	0.9977	0.9735	0.9867
	2	0.9653	0.9753	0.9783
3	1	0.9837	1.0735	1.0060
	2	0.9799	1.0234	0.9545
4	1	0.9446	1.0243	0.9874
	2	0.9816	1.0084	0.9794
5	1	0.9740	1.0340	1.0043
	2	0.9890	1.0414	1.0017
6	1	0.9763	1.0234	1.0029
	2	1.0012	0.9993	0.9765
7	1	0.9983	1.0602	0.9909
	2	0.9737	1.0495	1.0014
8	1	1.0020	1.0076	0.9756
	2	0.9990	1.0304	0.9717
9	1	1.0018	1.0178	1.0069
	2	0.9919	1.0330	1.0158
10	1	1.0162	0.9970	0.9919
	2	0.9919	0.9898	0.9783

*Corrected for flow and cylinder assay

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE 18. VARIABILITY OF GPT-NO NO_2 CALIBRATIONS

System	N*	Mean Slope	σ_e	σ_t	σ_{tot}**	Reproducibility
Control	10	0.9892	0.0158	0.0075	0.0175	0.0485
Volunteer	10	1.0212	0.0150	0.0219	0.0265	0.0735
Corrected Volunteer	10	0.9902	0.0140	0.0059	0.0152	0.0421

*N = number of participating volunteers

**$\sigma_{tot} = \sqrt{\sigma_e^2 + \sigma_t^2}$

Estimates of reproducibility were made for NO_2 calibrations using Equation 1-3; they are presented in Table 18. The control and corrected volunteer results show differences of less than 5 percent, 95 percent of the time, which represents only random effects. The volunteer results are slightly larger, less than 7 percent, 95 percent of the time due to the significant contribution of the equipment to the total variability.

Also given in Table 18 are the mean slope results for the NO_2 calibrations. When these means are compared to the theoretical value of 1.000, no significant differences are found. Therefore, the GPT-NO calibration procedure for NO_2 would be expected to give non-biased results and reproducibility of less than 7 percent, 95 percent of the time.

The analysis of variance for GPT-NO NO_2 calibrations is summarized in Appendix I.

EPA-287 (Cin.)
(4-76)

Summary of Conclusions from Variability Study of Gas Phase Titration With Excess Nitric Oxide Calibration Procedure

Ozone Calibrations by Gas Phase Titration with Excess Nitric Oxide--

In this study, the total variability of O_3 calibrations using the GPT-NO procedure is estimated by σ_{tot} (the standard deviation of the regression slopes, B_{ij}) given in Table 15. The term reproducibility defined in Equation 1-3 used σ_{tot} to determine the range where the difference between any two calibration slopes will fall 95 percent of the time. Reproducibility for calibrations employing the volunteer systems will be $\leq$ 10.5 percent of the mean slope, and those using the control system will be $\leq$ 6 percent of the mean slope. Referencing NO cylinder assays and flow standards to a central laboratory can reduce the reproducibility for the volunteer systems to $\leq$ 8.5 percent of the mean slope.

Total variability can be broken into two parts: a random component (σ_e) and a calibration system component (σ_t). The random components for O_3 calibrations using the volunteer systems or the control system were the same (about 2 percent of the mean slope). The calibration system component of variability (3 percent of the mean slope) for O_3 calibrations using the volunteer systems was statistically significant, and indicated that GPT-NO O_3 calibrations contain an equipment dependent bias. The calibration system component of variability for O_3 calibrations using the control system was statistically insignificant, demonstrating that operator contributions to the total variability cannot be separated from the random component. Besides the system dependent bias, the mean slope for O_3 calibrations using the volunteer systems was biased 7.5 percent higher than the UV reference system.

Our data indicates that a GPT-NO calibration system can be assembled that will give repeatable results. These calibrations differ from UV photometric calibrations by an amount which seems to be dependent on the equipment (+ 1 to + 15 percent). While the variability of O_3 calibrations using the GPT-NO procedure is acceptable, when coupled with the mean bias

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

as shown in this study, the GPT-NO procedure would be an unsatisfactory independent calibration procedure for reference methods for the determination of O_3 concentrations in the atmosphere.

Nitrogen Dioxide Calibrations by Gas Phase Titration with Excess Nitric Oxide--

The estimate of total variability (σ_{tot}) for NO_2 calibrations using the GPT-NO procedure is given in Table 18. Reproducibility for NO_2 calibrations was $\leq$ 7.4 percent of the mean slope when the volunteer systems were used, and $\leq$ 4.9 percent of the mean slope when the control system was used. If the cylinder assays and flow standards are referenced to a central laboratory, then the reproducibility of the volunteer systems is reduced to $\leq$ 4.2 percent of the mean slope.

The random components of variability for NO_2 calibrations using the volunteer and control systems are the same (about 1.5 percent of the mean slope). The calibration system component of variability (2 percent of the mean slope) for NO_2 calibrations using the volunteer systems contained an equipment dependent bias. However, the variability introduced by the equipment is less than ± 6 percent and the mean bias across the calibration equipment is zero. The calibration system component of variability for NO_2 calibrations using the control system was not statistically significant. As stated above, the mean slope for NO_2 calibrations using the GPT-NO volunteer systems showed no bias with respect to the reference system which was calibrated with an NBS NO_2 SRM.

In conclusion, the GPT-NO procedure is an acceptable independent calibration procedure for reference methods for the determination of NO_2 in the atmosphere.

SECTION 5

GAS PHASE TITRATION WITH EXCESS OZONE

INTRODUCTION

The gas phase titration with excess ozone (GPT-O_3) procedure is similar to the GPT-NO calibration procedure. Both are based upon the rapid gas phase reaction between O_3 and NO. The primary advantage of the former procedure is that it does not require an NO analyzer as is the case with the latter.

In the GPT-O_3 procedure, the output of an O_3 generator is assayed by adding a known amount of NO to excess O_3 in a dynamic reaction system. The dynamic system is designed to produce locally high concentrations of O_3 and NO in the reaction chamber with subsequent dilution to ensure complete NO reaction with relatively small chamber volumes. The reaction of NO with excess O_3 must be carefully controlled in order to obtain complete conversion of NO to NO_2 and also to minimize the reaction of O_3 with NO_2. This second and undesirable reaction is represented by

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \qquad (5\text{-}1)$$

and can give rise to errors in the assay of the O_3 concentration standard. Therefore, the method contains dynamic parameter and O_3 reduction specifications that ensure proper reaction conditions.

When O_3 is monitored by an uncalibrated O_3 analyzer, the resulting initial and final O_3 analyzer responses (I_o and I, respectively) are used together with the concentration of added NO to calculate the output of the O_3 generator ($[O_3]_{OUT}$). The following equation is used:

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3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

$$[O_3]_{OUT} = \frac{(I_o)}{(I_o)\left(\frac{F_O + F_D}{F_O + F_D + F_{NO}}\right) - (I)} \times [NO] \tag{5-2}$$

$$[O_3]_{OUT} \sim \frac{(I_o)}{(I_o - I)} \times [NO] \tag{5-3}$$

Additional O_3 concentrations required for calibration are obtained by diluting the output of the generator.

PRELIMINARY INVESTIGATION

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An investigation to evaluate the usefulness of the GPT-O_3 procedure for calibrating O_3 analyzers was conducted by the QAD, EMSL, EPA/RTP.

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Experimental

Test Atmosphere Generation--

A schematic diagram of a GPT system typical of those used in this study is shown in Figure 6. All surfaces in contact with reactant gases and reaction products are glass, Teflon®, or other non-reactive materials.

Ozone was continuously generated by UV irradiation of clean air passing through a quartz tube. The quantity of O_3 produced was controlled by a movable sleeve surrounding the UV lamp. A constant voltage transformer was used in conjunction with the UV lamp power supply to ensure stable output. The generator and its operating characteristics are described in detail by Hodgeson (9) and by the NBS (10).

Test Atmosphere Measurement--

Ozone was measured with a Bendix Model 8002 Chemiluminescence O_3 Monitor and with a Dasibi Model 1003-AH O_3 Analyzer (UV). The Dasibi was modified by replacing the analyzer's scrubber with a sample line connected

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

to a zero air source. The Bendix monitor was initially referenced to the Dasibi analyzer by allowing both analyzers to sample O_3 from a common manifold and then adjusting the span on the Bendix monitor to read the same O_3 concentration as measured by the Dasibi.

Nitric oxide and NO_2 measurements were made using a Bendix Model 8101-B NO_x Analyzer. The analyzer was modified by incorporating a Monitor Labs "Moly-Con" NO_x converter (Monitor Labs, Inc., San Diego, California).

Reagents--

Nitric oxide was obtained from NBS-SRM 1683a (45 ppm NO in N_2) and NO_2 was obtained from an NBS prototype NO_2 permeation device.

Results and Discussion

Verification of Dynamic Parameter and Ozone Reduction Specifications and Comparison of Ozone Measurements by Gas Phase Titration with Excess Ozone and Ultraviolet Photometry--

The GPT-O_3 procedure contains a dynamic parameter specification which controls the concentration and residence time of O_3 in the reaction chamber ($[O_3]_{RC}$ and t_R, respectively), and is defined as:

$$P_R = [O_3]_{RC} \times t_R = 1.5 \text{ ppm-min} \qquad (5\text{-}4)$$

The 1.5 ppm-min specification is based on empirical measurements by Rehme and Smith (unpublished data) using a GPT apparatus assembled from component parts and which was thought to be quite rigid. The procedure also contains an O_3 reduction specification of 75 to 80 percent (i.e., the amount of O_3 consumed by addition of NO during the GPT).

The validity of these specifications was verified using GPT reaction chambers of various sizes by substituting various values for P_R and performing repeated O_3 generator assays, adding NO in sufficient quantity to consume approximately 60, 70, 80, and 90 percent of the initial O_3

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

concentration. A Bendix NO_x Analyzer was used to monitor residual NO and resultant NO_2 during the GPT. The O_3 generator assays by GPT-O_3 were compared to corresponding O_3 measurements by UV photometry. Tests were conducted using reaction chamber volumes of 0.200 l and 0.500 l with P_R values of 1.4, 1.5, and 1.6 and a total flowrate of 1.5 l/min. The data is presented in Table 19.

In general, for a given reaction volume and value of P_R, the O_3 concentration assayed by GPT-O_3 ($[O_3]_{OUT}$) and the corresponding $[O_3]_{OUT}:[O_3]_{UV}$ ratio increase as the amount of O_3 consumed during GPT is increased. This trend is in qualitative agreement with the expected results: at lower levels of O_3 consumed, a low assay is expected due to reaction of residual O_3 with product NO_2; at higher levels of O_3 consumed, a high assay is expected due to incomplete reaction of NO with the available O_3. Conversely, for a given reaction volume and level of O_3 consumed, the O_3 assay and $[O_3]_{OUT}:[O_3]_{UV}$ ratio decrease as the value of P_R is increased. Again, this trend is in qualitative agreement with the expected results: as the value of P_R is increased, quantitative reaction of NO with O_3 and reaction of residual O_3 with product NO_2 both become more favorable and lead to lower O_3 assays.

While the qualitative nature of the data in Table 19 is consistent with the expected results, the quantitative results are less clear. The measured $[O_3]_{OUT}:[O_3]_{UV}$ ratios were always greater than 1.00 even when the GPT conditions would be expected to give ratios less than 1.00 (e.g., at high P_R and low O_3 consumed values). The reasons for this apparent positive bias are not fully understood. However, the data indicate a trend towards a 1:1 agreement with increasing P_R. This suggests that the optimum P_R (defined as the P_R value that results in an $[O_3]_{OUT}:[O_3]_{UV}$ = 1.00) for the GPT systems used in this study is somewhat higher than the previously reported value of 1.5. Calculations based on the data in Table 19 indicate that a ratio of 1.00 would be expected for the GPT systems used here at a P_R of approximately 1.8 when 75 to 80 percent of the available O_3 is consumed. The difference between these results (optimum P_R

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TABLE 19. VERIFICATION OF DYNAMIC PARAMETER AND O_3 REDUCTION SPECIFICATIONS AND COMPARISON OF O_3 BY GPT-O_3 AND UV PHOTOMETRY

$[O_3]_{OUT}$ (ppm)	$[O_3]_{UV}$ (ppm)	$\frac{[O_3]_{OUT}}{[O_3]_{UV}}$	P_R (ppm-min)	$[NO]_{OUT}$ (ppm)	$[NO_2]$ (ppm)	$\frac{[NO_2]^*}{[NO]_{OUT}}$	$[NO]_{Residual}$ (ppm)	O_3 Consumed (%)	V_{RC} (cm^3)
0.4233	0.403	1.050	1.467	0.2626	0.245	0.933	0.000	62.0	200
0.4277	0.403	1.061	1.473	0.2956	0.282	0.954	0.000	69.1	200
0.4260	0.403	1.057	1.457	0.3315	0.323	0.980	0.002	77.8	200
0.4322	0.403	1.072	1.464	0.3812	0.375	0.999	0.006	88.2	200
0.4161	0.401	1.038	1.520	0.2625	0.247	0.940	0.000	63.1	200
0.4183	0.401	1.043	1.516	0.3015	0.289	0.959	0.000	72.0	200
0.4188	0.401	1.044	1.505	0.3436	0.337	0.987	0.002	82.0	200
0.4270	0.401	1.065	1.522	0.3876	0.380	0.998	0.007	90.7	200
0.4124	0.398	1.036	1.648	0.2580	0.238	0.923	0.000	62.6	200
0.4111	0.398	1.033	1.630	0.2964	0.283	0.955	0.000	72.1	200
0.4106	0.398	1.032	1.613	0.3404	0.333	0.978	0.000	82.9	200
0.4210	0.398	1.058	1.639	0.3819	0.374	0.992	0.005	90.7	200
0.4210	0.404	1.042	1.458	0.2553	0.234	0.916	0.000	60.6	500
0.4241	0.404	1.050	1.461	0.2971	0.280	0.949	0.002	70.0	500
0.4272	0.404	1.057	1.465	0.3373	0.323	0.975	0.006	79.0	500
0.4385	0.404	1.085	1.495	0.3843	0.363	0.978	0.013	87.6	500
0.4205	0.408	1.031	1.565	0.2534	0.234	0.923	0.000	60.3	500
0.4194	0.408	1.028	1.552	0.2981	0.283	0.956	0.002	71.1	500
0.4231	0.408	1.037	1.558	0.3380	0.325	0.976	0.005	79.9	500
0.4312	0.408	1.057	1.580	0.3773	0.363	0.994	0.012	87.5	500
0.4190	0.413	1.015	1.666	0.2536	0.239	0.942	0.000	60.5	500
0.4190	0.413	1.015	1.657	0.2952	0.286	0.975	0.002	70.5	500
0.4238	0.413	1.026	1.666	0.3376	0.330	0.989	0.004	79.7	500
0.4298	0.413	1.041	1.681	0.3787	0.372	1.012	0.011	88.1	500

*$[NO]_{OUT}$ values corrected for $[NO]_{Residual}$

of 1.8) and those of Rehme and Smith (optimum P_R of 1.5) might be indicative of GPT system induced effects on GPT-O_3 calibrations. The dynamic parameter may, in fact, compensate for a bias resulting from other unknown causes.

Additional assays were performed using reaction chamber volumes of 0.700 l and 2.000 l with P_R values of 1.5 and 1.7 (see Table 20). The results with the 0.700 l reaction chamber were similar to those obtained with 0.200 l and 0.500 l volumes. Testing of a 2.00 l chamber yielded significantly higher $[O_3]_{OUT}:[O_3]_{UV}$ values in conjunction with significantly higher residual NO values, indicating error may be associated with calculating residence time (t_R) using the measured chamber volume (V_{RC}) and the reactant gas flowrates (F_O and F_{NO}). The actual residence time in this relatively large reaction chamber is probably significantly less and dependent on the flow dynamics in the chamber.

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Nitric Oxide and Nitrogen Dioxide Measurements During Gas Phase Titration with Excess Ozone--

In the gas phase titrations using the 0.200 l and 0.500 l reaction chambers and P_R values of 1.4, 1.5, and 1.6, the amount of residual NO ranged from 0.000 to 0.006 ppm when 75 to 80 percent of the available O_3 was titrated. The $[NO_2]:[NO]_{OUT}$ ratios for these titrations ranged from 0.975 to 0.989 when the $[NO]_{OUT}$ values were corrected for the small amount of residual NO. Thus, the amount of NO_2 generated during GPT under these conditions agreed favorably (within about 2 percent) with the amount of NO reacted.

When less than 75 percent of the O_3 was titrated, residual NO values were 0.002 ppm or less, but the $[NO_2]:[NO]_{OUT}$ ratios were as low as 0.92. This result indicates significant NO_2 losses by reaction with residual O_3. As mentioned earlier, under these conditions $[O_3]_{OUT}:[O_3]_{UV}$ ratios lower than 1.00 would be expected, but only values above 1.00 were actually obtained. Thus, the NO_2 data seems to support the existence of a positive bias in the GPT O_3 measurements. When more than 80 percent of the O_3 was titrated, residual NO values became significant, but the $[NO_2]:[NO]_{OUT}$

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TABLE 20. $[O_3]_{GPT\text{-}O_3}$ ASSAYS USING 700 AND 2000 CM^3 REACTION CHAMBERS

$[O_3]_{OUT}$ (ppm)	$[O_3]_{UV}$ (ppm)	$\frac{[O_3]_{OUT}}{[O_3]_{UV}}$	P_R (ppm-min)	$[NO]_{OUT}$ (ppm)	$[NO_2]$ (ppm)	$\frac{[NO_2]^*}{[NO]_{OUT}}$	$[NO]_{Residual}$ (ppm)	O_3 Consumed (%)	V_{RC} (cm^3)
0.4183	0.403	1.038	1.556	0.2481	-†	-	0.000	59.3	700
0.4155	0.403	1.031	1.539	0.2990	-	-	0.000	72.0	700
0.4210	0.403	1.045	1.549	0.3703	-	-	0.002	87.9	700
0.4282	0.403	1.063	1.572	0.3980	-	-	0.008	92.9	700
0.4516	0.400	1.129	1.713	0.2642	0.238	0.918	0.005	58.5	2000
0.4510	0.400	1.128	1.706	0.3304	0.304	0.949	0.010	73.2	2000
0.4607	0.400	1.152	1.739	0.3709	0.338	0.961	0.019	80.5	2000
0.4674	0.400	1.168	1.762	0.4066	0.369	0.972	0.027	87.0	2000
0.4645	0.400	1.161	1.751	0.4088	0.369	0.966	0.027	88.0	2000

*$[NO]_{OUT}$ values corrected for $[NO]_{Residual}$

†No data - instrument failure

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ratios approached 1.000, indicating excellent agreement between NO_2 generated and NO reacted.

Summary of Conclusions from Preliminary Investigation of Gas Phase Titration with Excess Ozone Calibration Procedure

The optimum dynamic parameter specification for GPT-O_3 calibrations appears to be system dependent. Optimum dynamic parameter, defined as the P_R value for which $[O_3]_{GPT-O_3}:[O_3]_{UV}$ ratio is 1.00, varied from 1.5 to 1.8 for the calibration systems studied.

Using the reaction chamber volume and flowrates to estimate residence time can lead to incorrect calibrations for certain types of reaction chambers. Residence time depends on the flow dynamics through the reaction chamber and not just the chamber volume.

Ozone calibrations can be performed using the GPT-O_3 procedure, provided the initial O_3 present is reduced by 75 to 80 percent. The ratio of $[O_3]_{GPT-O_3}$ to $[O_3]_{UV}$ varied from 1.026 to 1.057 for calibrations carried out with this restriction on O_3 reduction. Nitrogen dioxide produced during these calibrations agreed to within 2 percent of the NO consumed, indicating that little NO_2 is reacting with O_3.

One must be very careful when performing GPT-O_3 calibrations because even under conditions which limit side reactions and consume all available NO, the procedure still assays O_3 concentrations higher than does the UV photometric procedure.

VARIABILITY STUDY

A study was conducted to determine the variability of the GPT-O_3 calibration procedure. The GPT-O_3 calibration procedure used in the study can be found in Appendix C of this report. Ten operators with varying degrees of experience were selected for participation in the variability study.

Consideration was given to prior experience with GPT systems and to the type of GPT they were familiar with.

Experimental

Equipment--

Volunteer Gas Phase Titration Systems--The volunteers were instructed to furnish a GPT calibration system for the study. Each GPT system consisted of a clean air supply, a GPT reaction and dilution system, an NO standard, and various flow measurement devices. A Bendix Model 8002 Chemiluminescence Ozone Analyzer was supplied to individual volunteers. Test protocol required that the GPT system produce an O_3 output of 0.4 ppm at 1.5 l/min.

A listing of the volunteers who participated and their respective equipment is given in Appendix F.

Reference System--The reference system consisted of an O_3 generation system and a Dasibi Model 1003-AH O_3 Analyzer. The three chemiluminescence O_3 analyzers were eliminated from the reference system in this study, because the UV photometer and O_3 analyzers had always agreed in the two previous variability studies. The Dasibi was modified by removing the scrubber and by supplying clean air for the reference portion of the measurement cycle. Temperature and pressure readings were recorded for each Dasibi measurement. These readings enabled the experimenters to make corrections for each UV data set. A more complete description of the components in the reference system is available in Appendix H.

Control System--The control system (see Figure 11) was assembled from components meeting the GPT-O_3 procedural specifications. For a further description of components see Appendix H.

Zero Air Supply and Cleanup System--Clean air for all test systems was obtained by passing house compressed air through a particle trap to remove

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EPA-287 (Cin.)
(4-76)

oil and water droplets, and through an MSA Ultra Filter® to remove particulates. The air was then passed through a Permapure Dryer® and an indicating silica gel trap to remove moisture, through a pressure regulator into an ozonator to convert any NO to NO_2, and finally through activated charcoal and molecular sieve to remove NO_2 and HC.

Nitrogen Dioxide Permeation System--The NO_2 channel of an NO_x analyzer was calibrated using an NBS-SRM NO_2 permeation device (No. 1629). See Figure 12 for a schematic diagram. A description of the components within the system is given in Appendix H.

Reference Flow Measurement Equipment--Flow measurements made during calibration runs using the volunteer GPT systems were checked with a wet-test meter referenced to a 600-l spirometer and with NBS referenced bubble flowmeters. All measurements were corrected to 760 mm and 25° C. Soap-bubble and wet-test meter measurements were adjusted for water vapor corrections.

Nitric Oxide Standard Cylinder Analysis System--The assay of volunteer NO standards was performed using a Bendix Model 8101-C NO-NO_2-NO_x Analyzer operated on the 0 to 100 ppm range. The NO concentration of each standard was measured by direct comparison (without dilution) to two NBS-SRM's (No. 1683 and No. 1684).

Pretest Preparation--

Volunteers--Each volunteer was given a copy of the GPT-O_3 calibration procedure and instructed to verify that his GPT calibration system met the specifications given in the calibration procedure. Volunteers were encouraged to become familiar with the procedure by performing practice calibrations and applicable check-out procedures prior to participating in the study.

Test Laboratory--Following the initial set-up of all test laboratory systems and equipment, appropriate calibration, certification, and check-out procedures were carried out to ensure that the performance of the test systems was suitable for the stated purpose of the study. These pretest operations and pertinent test data are summarized in Appendix G.

Test Procedure--

The test laboratory was arranged so that one volunteer using his own GPT system and one volunteer using the control GPT system could be scheduled simultaneously. All operating conditions for the control system were predetermined and prescribed in a volunteer data form. The test procedure for a given test run is given below:

- Test coordinator calibrates the reference O_3 system using a Dasibi UV O_3 photometer.
- Test coordinator calibrates an $NO\text{-}NO_2\text{-}NO_x$ monitor using an SRM reference NO cylinder for NO and a gravimetrically calibrated NO_2 permeation device for NO_2.
- Volunteer calibrates a chemiluminescence O_3 analyzer using the GPT-O_3 procedure with the volunteer supplied apparatus.
- Coordinator monitors NO and NO_2 at the equilibrium point of the GPT.
- Test coordinator verifies the flow measurements (F_{NO}, F_D, F_O and maximum F_D) immediately following operator calibrations.
- Volunteer's calibrated O_3 analyzer is used to measure the six different reference O_3 concentrations (0.00, 0.08, 0.16, 0.24, 0.32, and 0.40 ± 0.01 ppm) generated. Reference O_3 atmospheres were monitored simultaneously by the Dasibi in the reference system and the operator calibrated analyzer.
- Volunteer repeats the calibration and measuring procedures using the control GPT system. Flow measurements were not verified during calibration runs using the control system.

Each volunteer generated two sets of O_3 atmospheres using his own GPT system and two sets of O_3 atmospheres using the control GPT system. Nitric oxide standards were compared to NBS-SRM NO standards by means of a chemiluminescence NO analyzer to determine the reliability of the operator's assay. The NO assay procedure is given in Appendix H.

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Data Analysis and Discussion of Results

Ozone Calibrations by Gas Phase Titration with Excess Ozone--

The O_3 measurements obtained with the GPT-O_3 calibrated analyzers were compared with the simultaneous reference system O_3 measurements. Data from each comparison was subjected to a least squares linear regression analysis using Equation 1-1. Regression constants for the control and volunteer GPT systems are given in Tables 21 and 22. The intercepts of the regression equations (B_2) were examined statistically and found to be not significantly different than zero. Table 23 gives the slopes of the volunteer system calibrations corrected for reference flow measurements and NO cylinder assays made by the test coordinator.

An analysis of variance was performed on the regression slopes (B_1) from both the control and volunteer systems using the model defined by Equation 1-2. The results of the analysis of variance of the slopes for the control, volunteer, and corrected volunteer data are given in Table 24. The corrected volunteer data represents data from the volunteer systems with corrections applied for reference flow measurements and NO cylinder assays made by the test coordinator. The results of volunteer 3 on the control system and volunteer 5 on the volunteer system were discarded from the data sets, based on the large difference in slopes from run 1 to run 2. Therefore, Table 24 lists N = 9 volunteers for both the control and volunteer systems.

TABLE 21. REGRESSION CONSTANTS FOR GPT-O_3 CONTROL SYSTEM CALIBRATION RUNS

Volunteer	Run	Slope	σ_{Slope}	Intecept	σ_{Int}	R^2	Slope (no int)
1	1	1.0254	0.0030	-0.0011	0.0007	1.0000	1.0217
	2	1.0202	0.0023	-0.0010	0.0006	1.0000	1.0168
2	1	1.0125	0.0011	0.0002	0.0003	1.0000	1.0130
	2	0.9939	0.0016	-0.0002	0.0004	1.0000	0.9931
3	1	0.9469	0.0016	0.0002	0.0004	1.0000	0.9474
	2	1.0381	0.0044	-0.0020	0.0011	0.9999	1.0314
4	1	1.0383	0.0011	-0.0001	0.0003	1.0000	1.0379
	2	1.0714	0.0024	0.0005	0.0006	1.0000	1.0732
5	1	1.0376	0.0027	-0.0010	0.0006	1.0000	1.0340
	2	1.0212	0.0025	-0.0008	0.0006	1.0000	1.0185
6	1	1.0234	0.0019	0.0012	0.0005	1.0000	1.0274
	2	1.0188	0.0017	-0.0007	0.0004	1.0000	1.0163
7	1	1.0120	0.0010	-0.0002	0.0002	1.0000	1.0112
	2	1.0202	0.0014	-0.0005	0.0003	1.0000	1.0184
8	1	1.0155	0.0022	-0.0008	0.0005	1.0000	1.0184
	2	1.0068	0.0012	0.0005	0.0003	1.0000	1.0085
9	1	1.0441	0.0015	0.0002	0.0004	1.0000	1.0447
	2	1.0356	0.0011	-0.0001	0.0003	1.0000	1.0352
10	1	1.0179	0.0022	-0.0005	0.0005	1.0000	1.0161
	2	1.0106	0.0015	-0.0003	0.0004	1.0000	1.0097

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TABLE 22. REGRESSION CONSTANTS FOR GPT-O_3 VOLUNTEER SYSTEM CALIBRATION RUNS

Volunteer	Run	Slope	σ_{Slope}	Intercept	σ_{Int}	Run	Slope (no int)
1	1	1.0563	0.0020	-0.0002	0.0005	1.0000	1.0556
	2	1.0722	0.0027	-0.0006	0.0007	1.0000	1.0700
2	1	1.1259	0.0047	0.0011	0.0012	0.9999	1.1296
	2	1.2038	0.0027	-0.0004	0.0007	1.0000	1.2024
3	1	1.0824	0.0019	0.0007	0.0005	1.0000	1.0848
	2	1.1177	0.0030	0.0011	0.0007	1.0000	1.1216
4	1	1.0756	0.0039	0.0009	0.0009	0.9999	1.0788
	2	1.0562	0.0011	0.0004	0.0003	1.0000	1.0575
5	1	1.2523	0.0025	0.0007	0.0006	1.0000	1.2547
	2	1.0412	0.0016	0.0006	0.0004	1.0000	1.0433
6	1	1.1929	0.0011	-0.0003	0.0003	1.0000	1.1919
	2	1.0939	0.0018	0.0007	0.0004	1.0000	1.0963
7	1	1.0010	0.0032	0.0035	0.0008	1.0000	1.0131
	2	1.0110	0.0022	0.0010	0.0005	1.0000	1.0145
8	1	1.0911	0.0037	0.0015	0.0009	1.0000	1.0961
	2	1.0738	0.0022	0.0018	0.0005	1.0000	1.0797
9	1	1.1451	0.0015	0.0003	0.0004	1.0000	1.1460
	2	1.0790	0.0020	0.0020	0.0005	1.0000	1.0860
10	1	0.9690	0.0011	-0.0004	0.0003	1.0000	0.9676
	2	0.9699	0.0013	-0.0003	0.0003	1.0000	0.9690

EPA-287 (Cin.)
(4-76)

TABLE 23. GPT-O_3 SUPPLEMENTAL MEASUREMENTS AND CORRECTED CALIBRATION SLOPES FOR VOLUNTEER SYSTEMS

Volunteer	Run	NO (Vol) / NO (Ref)	Flow (Vol) / Flow (Ref)	Corrected Factor	Slope Corrected for Flow and Cyl. Assay
1	1	1.011	0.9893	1.0002	1.0565
	2		0.9886	0.9995	1.0717
2	1	1.001	0.9862	0.9872	1.1115
	2		1.0024	1.0034	1.2079
3	1	0.9840	1.0141	0.9979	1.0801
	2		0.9876	0.9718	1.0862
4	1	1.000	0.9890	0.9890	1.0638
	2		0.9962	0.9962	1.0522
5	1	1.005	0.9906	0.9956	1.2468
	2		0.9940	0.9990	1.0402
6	1	0.9859	0.9944	0.9804	1.1695
	2		0.9950	0.9810	1.0731
7	1	1.006	1.0703	1.0767	1.0778
	2		1.0609	1.0673	1.0790
8	1	0.9761	1.0057	0.9817	1.0711
	2		0.9959	0.9721	1.0438
9	1	0.9990	0.9868	0.9856	1.1288
	2		0.9904	0.9894	1.0676
10	1	0.9940	1.1136	1.1069	1.0726
	2		1.1115	1.1048	1.0715

TABLE 24. VARIABILITY OF GPT-O_3 OZONE CALIBRATIONS

System	N*	Mean Slope	σ_e	σ_t	σ_{tot}**	Reproducibility
Control	9	1.0236	0.0106	0.0139	0.0179	0.0496
Volunteer	9	1.0787	0.0354	0.0568	0.0669	0.1854
Corrected Volunteer	9	1.0880	0.0361	0.0221	0.0423	0.1172

*N = number of participating volunteers

**$\sigma_{tot} = \sqrt{\sigma_e^2 + \sigma_t^2}$

Table 24 shows that O_3 calibrations performed with the control system have a random component of variability (σ_e = 0.0106) of about ± 1 percent of the mean slope. The calibration system component of the variability (σ_t = 0.0139) is statistically significant and is about ± 1.5 percent of the mean slope. These results differ slightly from those obtained in the GPT-NO variability study where the operators made no significant contribution to the total variability. However, the total variability (σ_{tot} = 0.0179) for the GPT-O_3 calibrations including operator effects is still less than ± 2 percent.

Random variability (σ_e = 0.0354) for O_3 calibrations performed with the volunteer systems is much larger than for the control system and is about ± 3.5 percent of the mean slope. The calibration system variability (σ_t = 0.0568) is also considerably larger at about ± 5.5 percent of the mean slope. The larger σ_t cannot be solely attributed to operator effects; therefore, the GPT-O_3 calibration systems make a contribution to the total variability (σ_{tot} = 0.0669) of about 6.5 percent of the mean slope.

Reproducibility for the GPT-O_3 systems at the 95 percent confidence level is given in the last column of Table 24. The maximum difference between the slopes of any two calibrations was $\leq$ 18.5 percent for volunteer GPT-O_3 systems. If NO standards and flow measurements were referenced to a central laboratory, the reproducibility could be reduced to ± 11.7 percent of the mean slope. Reproducibility for the control system was $\leq$ 4.9 percent of the mean slope at the 95 percent confidence level.

Besides having considerable variability, the results from GPT-O_3 systems show a mean bias. The mean slope for the control system calibration comparisons was 1.0236 (see Table 24). When compared to the theoretical value of 1.0000, this discrepancy is statistically significant. The value for the volunteer systems was 1.0787. Again, this slope is statistically different than 1.0000. Thus, the mean results from GPT-O_3 calibrations are biased 8 percent higher with respect to the UV reference system.

Corrections for reference flow measurements and NO cylinder assays were applied to the volunteer data to obtain corrected volunteer data. The random variability ($\sigma_e = 0.0361$) for the corrected slopes was unchanged at ± 3.5 percent of the mean slope; the calibration system variability ($\sigma_t = 0.0221$) was not statistically significant but at ± 2 percent of the mean slope is larger than the σ_{tot} for the control system. Corrections for the reference flow measurements and cylinder assay reduce the calibration system component of variability, and leave random error as the only statistically significant contribution to the total variability. The total variability for the GPT-O_3 corrected calibrations is still larger than the uncorrected GPT-NO calibrations ($\sigma_{tot} = 0.0423$ for GPT-O_3 corrected and $\sigma_{tot} = 0.0383$ for GPT-NO uncorrected).

The analysis of variance for GPT-O_3 ozone calibrations is summarized in Appendix I.

Nitric Oxide and Nitrogen Dioxide Measurements During Gas Phase Titration--

Added NO ($[NO]_{OUT}$), residual NO ($[NO]_{RES}$), and NO_2 generated ($[NO_2]_{GEN}$) values during calibrations using the volunteer GPT systems are compiled in Table 25. The data indicates a mean $[NO_2]_{GEN}:[NO]_{OUT}$ of 0.95 ± 0.07

TABLE 25. $[NO]_{OUT}$ AND $[NO]_{RESIDUAL}$ MEASUREMENTS FROM VOLUNTEER SYSTEM CALIBRATIONS

Volunteer Number	Run	$[NO]_{OUT}$ (ppm)	$[NO]_{RES}$ (ppm)	$[NO_2]_{GEN}$ (ppm)	$\frac{[NO_2]^{\dagger}_{GEN}}{[NO]_{OUT}‡}$
1	1	0.274	0.003	*	*
	2	0.287	0.003	*	*
2	1	0.320	*	*	*
	2	0.323	*	*	*
3	1	0.347	*	*	*
	2	0.351	0.001	0.305	0.866
4	1	0.340	0.000	0.345	1.015
	2	0.338	0.005	0.325	0.947
5	1	0.383	0.0025	0.3688	0.957
	2	0.337	0.000	0.343	1.018
6	1	0.3555	0.000	0.3225	0.907
	2	0.3517	0.002	0.353	0.999
7	1	0.318	0.009	0.358	0.911
	2	0.323	0.002	0.340	1.046
8	1	0.359	0.002	0.305	0.844
	2	0.358	0.000	0.293	0.818
9	1	0.361	0.001	0.340	0.939
	2	0.361	0.002	0.371	1.022
10	1	0.299	0.0013	0.305	1.017
	2	0.299	0.0003	0.301	0.997

†$[NO_2]_{GEN}/[NO]_{OUT}$ Mean ± 1 S.D. = 0.95 ± 0.07

‡$[NO]_{OUT}$ corrected for $[NO]_{RES}$

*No data — equipment malfunction

(mean ± 1 S.D.). By comparison, results obtained in the preliminary GPT-O_3 evaluation showed an $[NO_2]_{GEN}:[NO]_{OUT}$ ratio of 0.98 ± 0.01 at 80 percent O_3 consumed. The increased variability of the volunteer systems over the single laboratory system reflects the GPT-O_3 systems' contribution to variability. Residual NO was minimal with the exception of volunteer 7, run 1.

Summary of Conclusions from Variability Study of Gas Phase Titration with Excess Ozone Calibration Procedure

Reproducibility for GPT-O_3 calibrations using the volunteer systems was $\leq$ 18.5 percent of the mean slope, and for calibrations using the control system was $\leq$ 5 percent of the mean slope. Referencing NO cylinder assays and flow standards to a central laboratory can reduce the reproducibility for the volunteer systems to $\leq$ 11.5 percent of the mean slope.

Total variability can be broken into two parts: a random component (σ_e) and a calibration system component (σ_t). The random component for O_3 calibrations using the control system was 1.1 percent of the mean slope compared to a σ_e of 3.5 percent of the mean slope for the volunteer O_3 calibrations.

The calibration system component of variability (5.5 percent of the mean slope) for O_3 calibrations using the volunteer systems was statistically significant and showed that GPT calibration systems in use today can lead to biased O_3 calibrations. The σ_t for O_3 calibrations using the control system was also statistically significant and showed that operator contributions to the total variability are about 1.5 percent of the calibration slope.

Besides the considerable system induced variability, the mean slope for O_3 calibrations using the volunteer systems was biased 8 percent higher with respect to the UV photometric reference system. The large difference in performance between the control and volunteer systems demonstrated that a GPT calibration system can be assembled yielding low variability and differing from UV photometric calibrations by only 2 to 3 percent, but the majority of the GPT systems in this study could not achieve similar results.

EPA-287 (Cin.)
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We conclude that the design and construction of the GPT calibrators in use today need considerable improvement. With the large variability and mean bias shown in this study, the GPT-O_3 procedure would be an unsatisfactory independent calibration procedure for reference methods for the determination of O_3 concentrations in the atmosphere.

ADDITIONAL STUDY

At the conclusion of the GPT-O_3 variability study an additional study was conducted to determine the effect of using the uncalibrated O_3 analyzer to establish the initial O_3 concentration as specified in the procedure. The dynamic parameter specification given in the procedure is based on the concentration and residence time of O_3 in the GPT reaction chamber ($P_R = [O_3]_{RC} \times t_R = 1.5$). If the O_3 analyzer is initially out of calibration, the actual O_3 concentration established at the start of the GPT might be significantly different than that indicated by the analyzer. Consequently, the actual value of P_R during the GPT would be different than the specified value of 1.5, and could, in turn, affect the accuracy of O_3 calibrations using the GPT-O_3 procedure.

To determine the magnitude of this effect, additional O_3 assays were performed employing the control GPT system used in the variability study and a Bendix Model 8851 GPT calibration system. Two O_3 analyzers were initially calibrated against the UV reference system. Flowrates were established in each of the GPT systems using the specified $P_R = 1.5$. In the first run, an O_3 concentration of 80 percent upper range limit (URL) (0.4 ppm) was generated and assayed by the GPT-O_3 procedure and by UV photometry (reference system). For succeeding runs, the O_3 analyzers were deliberately misspanned prior to generating the 80 percent URL concentration and making the required measurements. The flowrate conditions established for the first run (except for the NO flowrate) were maintained for subsequent runs. For each run, the O_3 concentration was determined by GPT-O_3 and UV photometry. The actual P_R for each run was calculated using the UV photometric O_3 measurement and the residence time in the reaction chamber. The test data are tabulated in Tables 26 and 27.

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TABLE 26. $[O_3]_{GPT\text{-}O_3}:[O_3]_{UV}$ RATIOS VERSUS P_R FOR CONTROL GPT SYSTEM*

Run	I_o (% chart)	I (% chart)	F_{NO} (cm^3/min)	[NO] (ppm)	$[O_3]_{GPT\text{-}O_3}$ (ppm)	$[O_3]_{UV}$ (ppm)	$\frac{[O_3]_{GPT\text{-}O_3}}{[O_3]_{UV}}$	P_R (ppm-min)
A	80.25	21.5	8.476	.2965	.405	.401	1.010	1.55
B	80.3	21.25	7.791	.2726	.371	.365	1.014	1.42
C	80.0	21.7	9.327	.3260	.447	.445	1.005	1.71
D	79.75	18.1	11.13	.3886	.503	.501	1.004	1.91
E	80.3	18.25	14.64	.5102	.660	.658	1.003	2.46
F	80.75	19.25	7.401	.2590	.340	.334	1.018	1.30
G	78.6	16.0	6.654	.2330	.293	.285	1.028	1.11
H	80.0	17.7	17.98	.6249	.802	.811	0.989	2.98
I	79.5	17.5	20.54	.7125	.914	.928	0.985	3.37
J	80.25	19.5	23.95	.8291	1.10	1.126	0.973	4.01
K	79.7	18.5	33.38	1.1485	1.50	1.575	0.949	5.35

*$[NO]_{STD}$ = 52.5 ppm
F_O = 318.2 cm^3/min.
$F_O + F_D$ = 1492.5 cm^3/min.
V_{RC} = 275 cm^3

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TABLE 27. $[O_3]_{GPT-O_3}$:$[O_3]_{UV}$ RATIOS VERSUS P_R FOR BENDIX GPT SYSTEM*

Run	I_o (% chart)	I (% chart)	F_{NO} (cm^3/min)	[NO] (ppm)	$[O_3]_{GPT-O_3}$ (ppm)	$[O_3]_{UV}$ (ppm)	$\frac{[O_3]_{GPT-O_3}}{[O_3]_{UV}}$	P_R (ppm-min)
A	78.75	22.25	9.77	.2924	.408	.394	1.036	1.60
B	79.2	21.8	9.05	.2709	.374	.360	1.039	1.47
C	79.7	17.9	11.93	.3565	.460	.442	1.041	1.77
D	80.0	19.4	13.31	.3974	.525	.510	1.029	2.02
E	80.5	17.8	11.00	.3289	.422	.410	1.029	1.65
F	79.75	17.3	18.14	.5398	.689	.672	1.025	2.60
G	79.25	16.25	9.15	.2739	.345	.330	1.045	1.34
H	79.25	17.3	7.80	.2337	.299	.289	1.035	1.19
I	80.4	18.9	21.00	.6238	.816	.802	1.016	3.05
J	78.7	18.9	24.01	.7118	.937	.928	1.010	3.47

*$[NO]_{STD}$ = 45.2 ppm

F_O = 295.4 cm^3/min.

$F_O + F_D$ = 1500.7 cm^3/min.

V_{RC} = 250 cm^3

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Graphical presentations of the data showing $[O_3]_{GPT-O_3}:[O_3]_{UV}$ ratios versus actual P_R for the control and Bendix GPT systems are given in Figures 13 and 14. In the control system, the $[O_3]_{GPT-O_3}:[O_3]_{UV}$ ratio changed by about 3.3 percent over a range of P_R values from 1.0 to 3.0. This range of P_R values corresponds to the O_3 analyzer being out of calibration by ± 50 percent. In the Bendix system, the ratio changed by about 2.5 percent over the same range of P_R values. Thus, the effect of the O_3 analyzer being out of calibration by ± 50 percent is only about 1 to 2 percent.

The results of this study also provide additional evidence that the optimum P_R for GPT systems is different from system to system. Figure 13 indicates that the optimum P_R for the control GPT system used here is approximately 2.35. However, the optimum P_R for the Bendix system is approximately 4.35 (Figure 14).

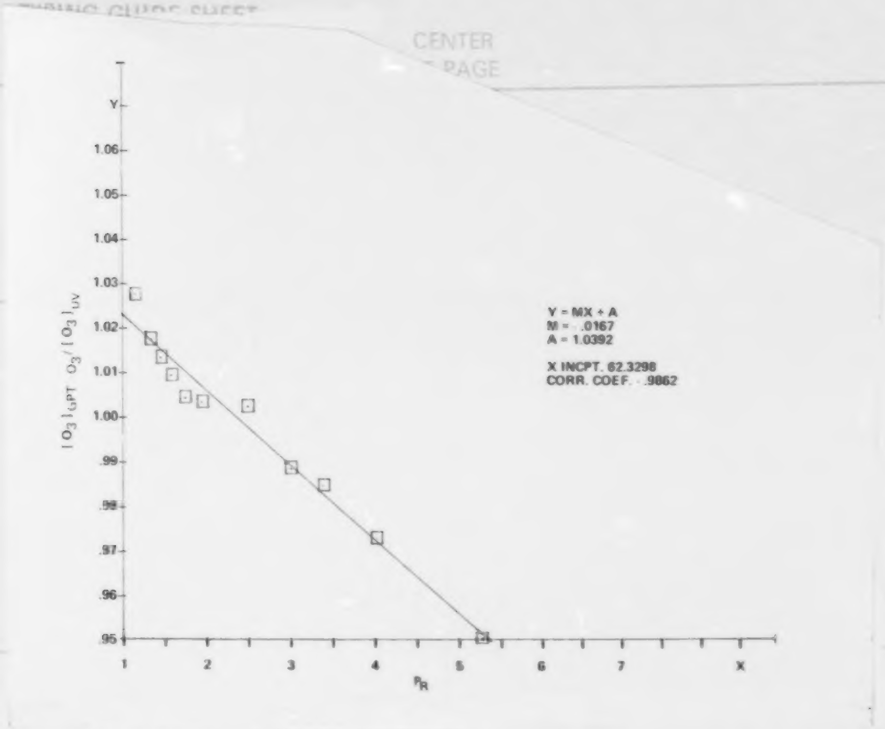

Figure 13. Least squares linear plot of $[O_3]_{GPT-O_3}:[O_3]_{UV}$ ratio versus P_R for control GPT system.

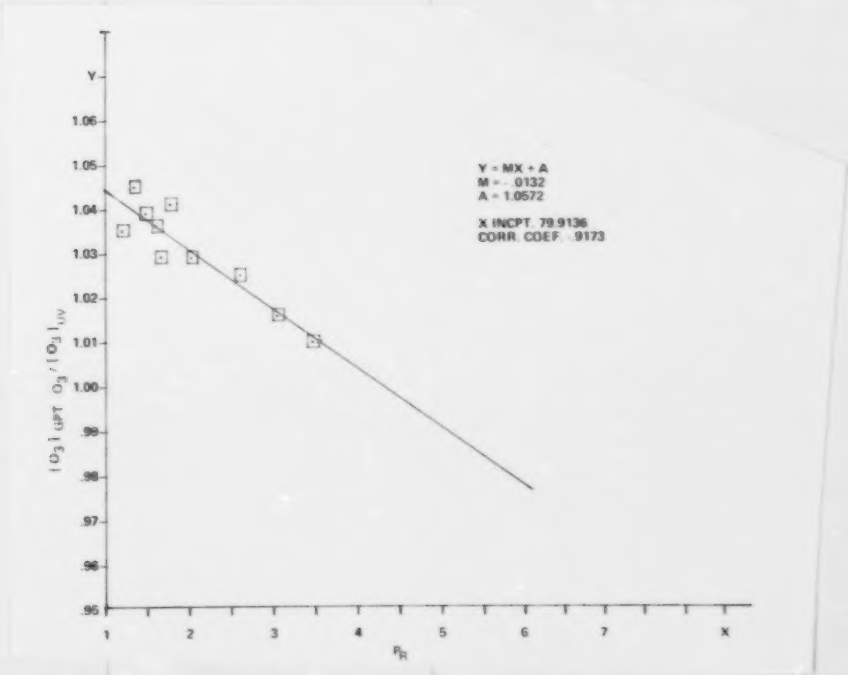

Figure 14. Least squares linear plot of $[O_3]_{GPT-O_3}:[O_3]_{UV}$ ratio versus P_R for Bendix GPT system.

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SECTION 6

BORIC ACID-POTASSIUM IODIDE (BAKI)

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INTRODUCTION

One of the potential replacements for the NBKI procedure uses a simple modification of the current procedure: a boric acid-buffered potassium iodide (BAKI) absorbing reagent is used rather than the phosphate-buffered reagent. The BAKI procedure is based upon the reaction between O_3 and potassium iodide (KI) to release iodine (I_2) according to the stoichiometric equation:

$$O_3 + 2I^- + 2H^+ \rightarrow I_2 + H_2O + O_2 \qquad (6\text{-}1)$$

The stoichiometry is such that the amounts of O_3 absorbed and I_2 released are equivalent. Ozone is absorbed in a 0.1 M boric acid solution containing 1 percent KI and the I_2 released is measured spectrophotometrically as the triiodide ion (I_3^-) at 352 nm. The output of a stable O_3 generator is assayed at several output settings and the generator is then used to calibrate the chemiluminescence O_3 analyzer. It is essential that the O_3 generator be used immediately after calibration and without physical movement. Recalibration must be conducted after each usage.

Considerable developmental work on this modified potassium iodide procedure was conducted by Flamm (13) while supported by an EPA grant (Grant #R803403). The results of Flamm's work indicate that BAKI is clearly superior to existing NBKI procedures in terms of accuracy and precision. Flamm reported that O_3 analysis with this procedure gave a consistent agreement with UV photometry over the concentration range of 0.1 to 3.5 ppm. The procedure was insensitive to such factors as absorber design and color

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development time. These variables were previously demonstrated to affect results with the NBKI procedure. Measurements by Paur (11) also indicated excellent agreement between BAKI and UV photometric techniques. However, in an earlier study, Hodgeson (7) found a significant positive bias (~ 8 percent) when he compared these two methods.

PRELIMINARY INVESTIGATION

Because of the positive bias reported by Hodgeson, an investigation to evaluate the BAKI procedure for calibrating O_3 monitors was conducted by QAD, EMSL, EPA/RTP.

Contrasting with the preliminary evaluations of the UV, GPT-NO, and GPT-O_3 procedures, the BAKI study employed four participants in a laboratory study in which the BAKI procedure was used to assay O_3 concentrations. For comparison purposes, these O_3 concentrations were also assayed using UV photometry.

The study was designed for simultaneous sampling from a common manifold by each of the four participants. A nominal O_3 concentration range of 0 to 0.6 ppm was investigated. Duplicate determinations at six concentration levels were obtained each day over a two day period. Thus, the total number of valid determinations possible was 96 (2 determinations x 4 participants x 6 concentrations x 2 days = 96).

A draft BAKI calibration procedure was prepared using a format similar to that used for the other tentative procedures previously published in the Federal Register O_3 notice (1). A copy of the draft procedure appears in Appendix D of this report.

Four individuals, all EMSL, EPA/RTP staff members, participated in the study. Each of the participants was given a copy of the draft BAKI procedure and asked to become familiar with the procedure and to assemble the required equipment.

Experimental

Test Atmosphere Generation--

An O_3 generation and distribution system was constructed from component parts. A diagram of the system is given in Figure 15. Purified house air was passed through an O_3 generator to generate the required O_3 concentrations. A Tylan mass flow controller and mass flowmeter were used to control the air flow through the O_3 generator. The air flowrate through the ozone generator was set at approximately 5 l/min.

The distribution manifold and all components downstream of the O_3 generator were constructed of glass. The first five ports of the manifold were used as sampling ports and all other ports were capped. Excess flow was vented into the room. Integrity of the manifold system was verified by generating an O_3 concentration of approximately 0.6 ppm and sampling at each of the five sample ports with a UV photometer.

Test Atmosphere Measurement--

Boric Acid-Potassium Iodide--All BAKI O_3 measurements were obtained according to the instructions given in the draft BAKI procedure (Appendix D). All samples were 10-minute samples and absorbers were rinsed with deionized water and drain-dried between determinations.

Each participant was responsible for assembling his own KI sampling train. Three of the participants used midget impingers for sample collection and one participant, by design, used "Mae West" absorbers. The technique of controlling and monitoring flow rates varied in each train. Documentation of the KI sampling trains is given in Table 28. Identical sections of Teflon® tubing (4.5 ft long, 0.25 in O.D.) were used to connect the KI sampling trains to the distribution manifold.

For reasons of convenience, a common set of reagents was prepared by the test coordinator according to the directions given in the draft BAKI procedure. A list of the reagents used and their sources is given

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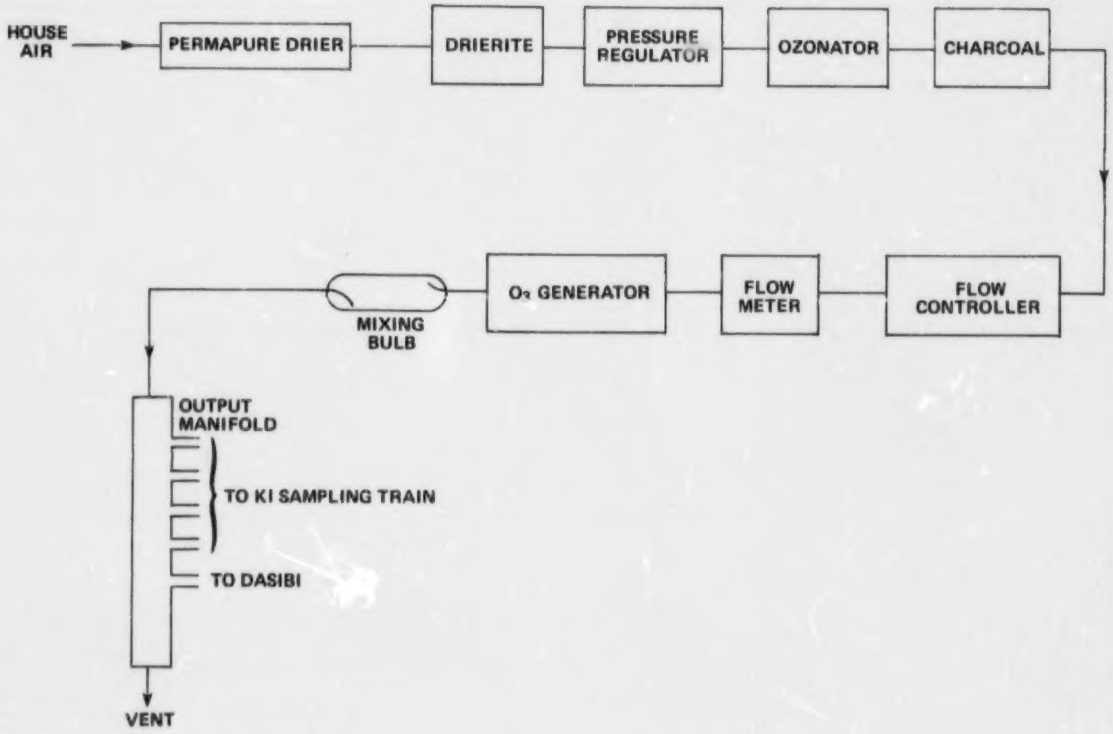
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PERMAPURE DRIER
DRIERITE
PRESSURE REGULATOR
OZONATOR
CHARCOAL
FLOW CONTROLLER
FLOW METER
O₃ GENERATOR
MIXING BULB
OUTPUT MANIFOLD
TO KI SAMPLING TRAIN
TO DASIBI
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Figure 15. Diagram of O_3 test generation and distribution system.

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE 28. COMPONENTS OF KI SAMPLING TRAINS

Participant	Absorber	Flow Control	Flow Monitoring	Flow Standard
1	Mae West	Vac. pump-vac. reg.-needle valve	Rotameter	Cal. wet-test meter
2	Midget impinger	Crit. orifice-vac. pump	None	Cal. wet-test meter
3	Midget impinger	House vac.-vac. reg.-needle valve	Mass flowmeter	Soap-bubble meter
4	Midget impinger	House vac.-vac reg.-mass flow controller	Mass flowmeter	Soap-bubble meter

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

in Table 29. All solutions were prepared using deionized water. Each participant was given a reagent bottle containing sufficient BAKI absorbing reagent to complete the tests. The test coordinator prepared and standardized 0.05 N I_2 solutions by both Methods A and B (see Appendix D).

Each participant furnished his own spectrophotometer and prepared a KI calibration curve according to the directions given in the draft BAKI procedure. A list of the spectrophotometers used by the participants is given in Table 30.

Ultraviolet Photometric Ozone Measurements--A Dasibi Model 1003-AH O_3 Analyzer (S/N 1674) was modified by removing the O_3 scrubber and by supplying zero air to the solenoid valve for the reference portion of the measurement cycle. A span factor of 50.750 was dialed into the instrument. A comparison was obtained with another modified Dasibi photometer (S/N 1137) that had been serving as one of the primary reference photometers for both EMSL and ESRL. The regression equation was:

$$[O_3]_{DAS\ (S/N\ 1674)} = 0.9824\ [O_3]_{DAS\ (S/N\ 1137)} - .0017\ \text{ppm} \qquad (6\text{-}2)$$

All O_3 measurements obtained with the Dasibi (S/N 1674) were corrected using the above equation.

Results and Discussion

Manifold Integrity Test--

Participants were assigned to individual sampling ports. The KI sampling trains were connected to the distribution manifold with identical sections of Teflon® tubing. The results of the manifold integrity test are tabulated in Table 31. These results show that O_3 concentrations at all sample ports were identical.

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TABLE 29. REAGENTS FOR BAKI PROCEDURE

Reagent	Manufacturer	Catalogue Number	Lot Number	Grade
Arsenious oxide	G. F. Smith	Certified primary standard	Certified primary standard	Certified primary standard
Boric acid	Fisher	A-74	753602	Certified ACS
Deionized water	Continental Deionized Water Service			
Iodine	Mallinckrodt	1008	SRY	Analytical reagent
Mercuric iodide	Matheson, Coleman & Bell	MX355 CB511	12	Reagent ACS
Potassium iodate	Fisher	SD-P-232	755634	Certified solution
Potassium iodide	Matheson, Coleman & Bell	PX1505 CB626	57	Reagent ACS
Sodium bicarbonate	Mallinckrodt	7412	WVRE	Analytical reagent
Starch	Fisher	S-516	784639	Certified ACS
Sulfuric acid	Fisher	A-300	783876	Reagent ACS

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TABLE 30. SPECTROPHOTOMETERS

Participant	Manufacturer	Model	S/N
1	Bausch & Lomb	100	410KY
2	Bausch & Lomb	710	1259XZ
3	Bausch & Lomb	100	284KV
4	Bausch & Lomb	100	176KS

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EPA-287 (Cin.)
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TABLE 31. MANIFOLD INTEGRITY TEST RESULTS*

	Port 1	Port 2	Port 3	Port 4	Port 5
	617	613	611	611	610
	607	612	608	613	616
	613	608	614	608	614
	612	607	614	611	611
	609	609	610	612	613
	608	613	612	616	609
	610	611	611	606	611
	612	621	610	613	609
	612	606	610	610	607
	613	612	608	607	611
AVE.	611.3	611.2	610.8	610.7	611.1

*O_3 concentration in ppb as measured with Dasibi photometer.

EPA-287 (Cin.)
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Potassium Iodide Calibration Curves--

The KI calibration data for each participant is listed in Table 32. The results show excellent agreement between the two I_2 standards (Methods A and B).

The required diluted I_2 standards were prepared by each participant from the 0.05 N I_2 standardized with arsenious oxide (As_2O_3) (Method A) that had been provided by the test coordinator. A diluted standard prepared from potassium iodate (KIO_3) (Method B) was then used by the participant to verify his individual KI calibration curve. The results of the I_2 standardization are given below:

Method A:

wt. primary standard As_2O_3 = 2.47185 g

$$\text{Normality} = \frac{(2.47185)}{(49.46)} = 0.049977\text{ N}$$

Titration of two 20.00-ml aliquots of As_2O_3 solution required 20.30 ml and 20.40 ml I_2 solution.

$$\text{Normality} = \frac{(20.00)\ (0.049977)}{(20.35)} = 0.04912\text{ N}$$

Method B:

50.00 ml of 0.1000 N KIO_3 (Fisher certified), 2 g of KI, and 10 ml of 1 N sulfuric acid (H_2SO_4) diluted to 100 ml.

$$\text{Normality} = \frac{(0.1000)\ (50)}{(100)} = 0.05000\text{ N}$$

Comparison of Boric Acid-Potassium Iodide and Ultraviolet Photometric Ozone Measurements--

At each concentration level, preliminary Dasibi measurements were made until a stable O_3 output from the generator was indicated. At a signal from the test coordinator, the participants then began sampling. Dasibi O_3

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TABLE 32. KI CALIBRATION DATA

			Participant			
Method A	Method B	μg O_3	1 Net Abs.	2 Net Abs.	3 Net Abs.	4 Net Abs.
0		0	0.000	0.000	0.000	0.000
1		2.358	0.123	0.128	0.121	0.125
2		4.716	0.246	0.249	0.249	0.245
3		7.073	0.374	0.373	0.369	0.374
4		9.431	0.498	0.499	0.494	0.498
5		11.789	0.623	0.627	0.621	0.630
	5	12.000	0.636	0.638	0.634	0.631
Method A sensitivity (Abs/μg O_3)			0.0529	0.0530	0.0526	0.0533
Method B sensitivity (Abs/μg O_3)			0.0530	0.0532	0.0528	0.0526

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measurements were obtained throughout the 10-minute sampling period. At the end of this period, sample absorbances were read and recorded on data forms, a test result (ppm O_3) calculated and submitted to the test coordinator, and the KI sampling train prepared for the next determination. The average O_3 concentration for the 10-minute sampling period as measured by the Dasibi was calculated from 25-27 individual readings. Ozone concentrations measured by the BAKI procedure and corresponding Dasibi O_3 concentrations are given in Table 33. The Dasibi data was referenced to Dasibi S/N 1137 by the following equation:

$$[O_3]_{DAS\ (S/N\ 1137)} = \frac{[O_3]_{DAS\ (S/N\ 1674)}}{0.9824} \tag{6-3}$$

Figure 16 shows the least squares regression plot for all 92 valid data points. The regression data is also summarized in Table 34.

The data indicate generally good agreement (± 5 percent) between O_3 concentrations measured by the BAKI procedure and UV photometry. When all 92 data points are combined, the following regression relationship results:

$$[O_3]_{BAKI} = 1.0117\ [O_3]_{DAS} + 0.0058\ \text{ppm} \tag{6-4}$$

These findings are in agreement with the earlier results of Flamm (11) and Paur (12). There was no evidence of a positive bias of the magnitude reported by Hodgeson (7).

The regression data for two of the participants (1 and 4) and for the combined data indicated a significant non-zero intercept. The individual BAKI data points (Sample No. 151, 152, 241, 242, in Table 33) also reflect this phenomenon. At the completion of the study, several BAKI O_3 determinations on the zero air source used in the study were obtained. The results of these measurements are given in Table 35 and indicate that the zero air source contains components equivalent to approximately 0.010 ppm O_3, which would account for the non-zero intercepts obtained in the study.

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE 33. BAKI O_3 CONCENTRATIONS AND CORRESPONDING DASIBI O_3 CONCENTRATIONS*

Sample No.	Participant 1	2	3	4	DASIBI**
111	0.564	--	0.619	0.570	0.573
112	0.594	0.608	0.609	0.587	0.575
121	0.454	0.484	0.489	0.469	0.448
122	0.456	0.479	0.487	0.459	0.447
131	0.075	0.068	0.072	0.069	0.068
132	0.077	0.073	0.068	0.073	0.069
141	0.341	0.350	0.354	0.347	0.344
142	0.351	0.366	0.308	0.351	0.343
151	0.016	0.001	0.000	0.006	0.000
152	0.010	0.001	0.000	0.012	0.000
161	0.210	0.209	0.206	0.211	0.198
162	0.204	0.209	--	0.207	0.198
211	0.088	0.105	0.078	0.076	0.069
212	0.076	0.071	0.074	0.076	0.069
221	0.451	0.472	0.467	0.461	0.450
222	0.427	0.470	0.459	0.440	0.451
231	0.212	0.212	0.206	0.211	0.198
232	0.204	0.211	0.206	0.211	0.198
241	0.012	0.000	0.000	0.006	0.000
242	0.008	0.000	0.003	0.006	0.000
251	0.354	0.360	0.355	0.348	0.348
252	0.338	0.361	0.362	0.350	0.348
261	0.548	NA	0.594	0.581	0.575
262	0.577	NA	0.594	0.574	0.573

*O_3 concentrations in ppm

**DASIBI O_3 concentrations referenced to DASIBI (S/N 1137) by:

$$[O_3]_{\text{DAS (S/N 1137)}} = \frac{[O_3]_{\text{DAS (S/N 1674)}}}{0.9824}$$

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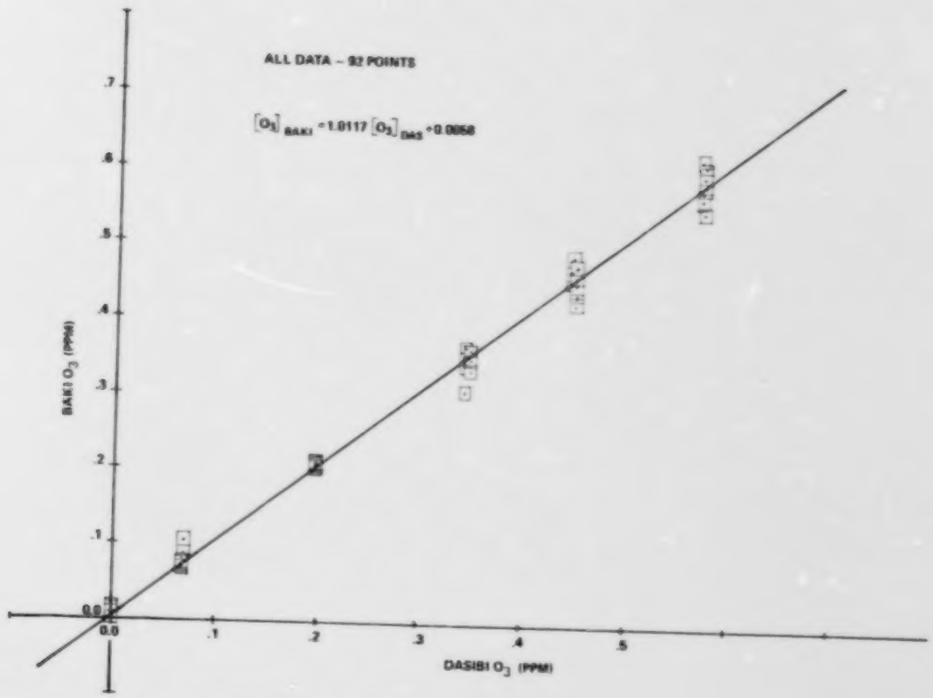

Figure 16. Comparison of BAKI and Dasibi O_3 measurements.

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EPA-287 (Cin.)
(4-76)

TABLE 34. REGRESSION DATA FOR BAKI O_3 MEASUREMENTS*

Participant	1	2	3	4	All Data
Slope	.9708	1.0479	1.0482	.9959	1.0117
Intercept	.0123	.0028	-.0017	.0077	.0058
Correlation coefficient	.9988	.9990	.9981	.9995	.9981
Upper 95% confidence interval (slope)	.9919	1.0705	1.0779	1.0098	1.0250
Lower 95% confidence interval (slope)	.9496	1.0254	1.0185	.9820	.9983

*$[O_3]_{BAKI}$ = slope $[O_3]_{DAS}$ + intercept

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE 35. BAKI O_3 MEASUREMENTS - ZERO AIR

Zero Air Source	Absorbers*	Gross Abs.	Reagent Abs.	Net Abs.	Equiv. [O_3] (ppm)
House	MW	.013	.004	.009	.017
House	MW	.010	.004	.006	.012
House	MW	.010	.006	.004	.008
House	MI	.010	.006	.004	.008
Cylinder	MW	.008	.004	.004	.008

*MW = Mae West absorbers

MI = Midget impingers

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PAGE NUMBER
EPA-287 (Cin.)
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Summary of Conclusions from Preliminary Investigation of Boric Acid-Potassium Iodide Calibration Procedure

The results revealed a generally good agreement (± 5 percent) between the BAKI and UV photometric procedures for the measurement of sub-ppm O_3 concentrations.

A ruggedness test subsequently performed by EMSL, EPA/RTP, indicated a problem with the BAKI procedure related to O_3 and/or I_2 demands by certain batches of BAKI absorbing reagent. Discussions with Flamm confirmed this phenomenon. Flamm also indicated that these demands, when present, can be satisfied by pretreatment of the absorbing reagent with hydrogen peroxide (H_2O_2) solution. A copy of the draft procedure (Appendix D) was given to Flamm for his comments and recommendations, especially in the area of O_3 and I_2 demand. The procedure was subsequently revised to incorporate an H_2O_2 pre-treatment procedure. A copy of the revised procedure can be found in Appendix E of this report.

VARIABILITY STUDY

A study was conducted to determine the variability of the BAKI O_3 calibration procedure. The BAKI calibration procedure as described in Appendix E of this report was used for the purpose of this study. This procedure is a revised version of the method investigated in the preliminary study.

Ten volunteers (operators) with varying degrees of experience participated in the study. Seven of the volunteers participated at EMSL, EPA/RTP. The remaining three volunteers participated at laboratories located outside of North Carolina. The ten volunteers who participated in the study and their affiliation are listed in Appendix F.

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EPA-287 (Cin.)
(4-76)

Experimental

Equipment--

Volunteer Boric Acid-Potassium Iodine Calibration Systems--Volunteers were instructed to furnish their own BAKI calibration apparatus consisting of a KI sampling train, a spectrophotometer, and flow measuring equipment. Reagents from a variety of commercial suppliers were provided to the RTP volunteers. Each of these volunteers was provided with a different combination of the necessary reagents: e.g., J. T. Baker KI, Fisher KIO_3, Mallinckrodt boric acid (H_3BO_3), etc. The three out-of-state volunteers were required to furnish their own reagents.

Reference System--The reference system consisted of an O_3 generation and sampling system, two UV photometers, and a dynamic AC line voltage regulator. The UV photometers were Dasibi Model 1003-AH O_3 Analyzers modified to operate as absolute photometers. A schematic diagram of the reference system is shown in Figure 17.

Zero Air Supply and Cleanup System--The zero air required for all test systems in the test laboratory was produced by first passing house compressed air into a particle trap to remove oil and water droplets, then through an MSA Ultra Filter® to remove particulates, through a pressure regulator, into an ozonator to convert any NO to NO_2, and finally through activated charcoal and molecular sieve to remove NO_2 and HC.

Reference Flow Measurement Equipment--Reference flow measurements were obtained using a calibrated Hastings mass flowmeter. The flowmeter was calibrated using a Hastings Miniflow Kit certified (NBS traceable) 1000-cm^3 bubble flowmeter. The calibration curve for the Hastings mass flowmeter is shown in Figure 18.

Pretest Preparation--

Volunteers--Each volunteer was given a copy of the BAKI O_3 calibration procedure and instructed to verify that his BAKI calibration system met the specifications given in the procedure. Volunteers were encouraged to become

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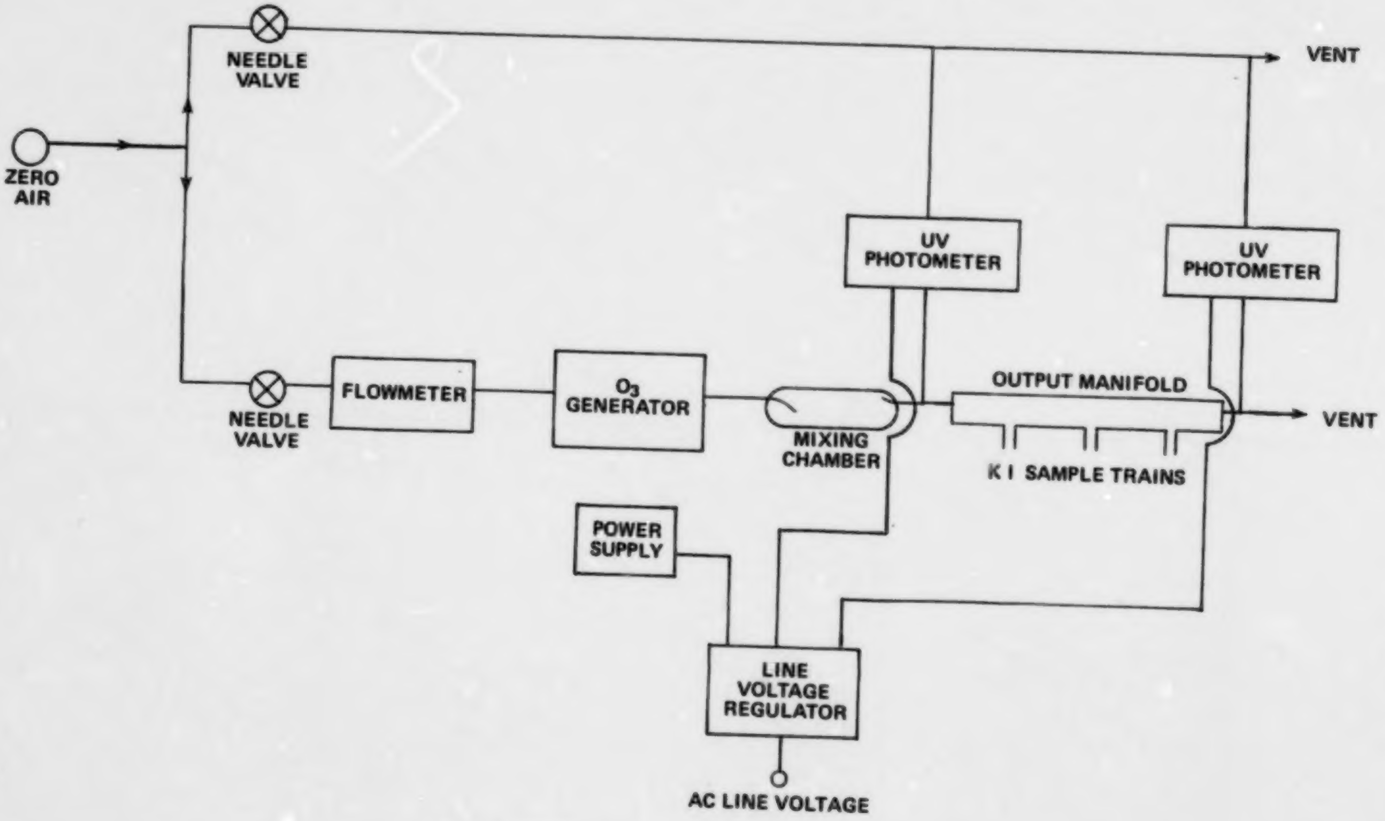
ZERO AIR
NEEDLE VALVE
NEEDLE VALVE
FLOWMETER
O_3 GENERATOR
MIXING CHAMBER
UV PHOTOMETER
UV PHOTOMETER
OUTPUT MANIFOLD
K I SAMPLE TRAINS
VENT
VENT
POWER SUPPLY
LINE VOLTAGE REGULATOR
AC LINE VOLTAGE

Figure 17. Diagram of reference system.

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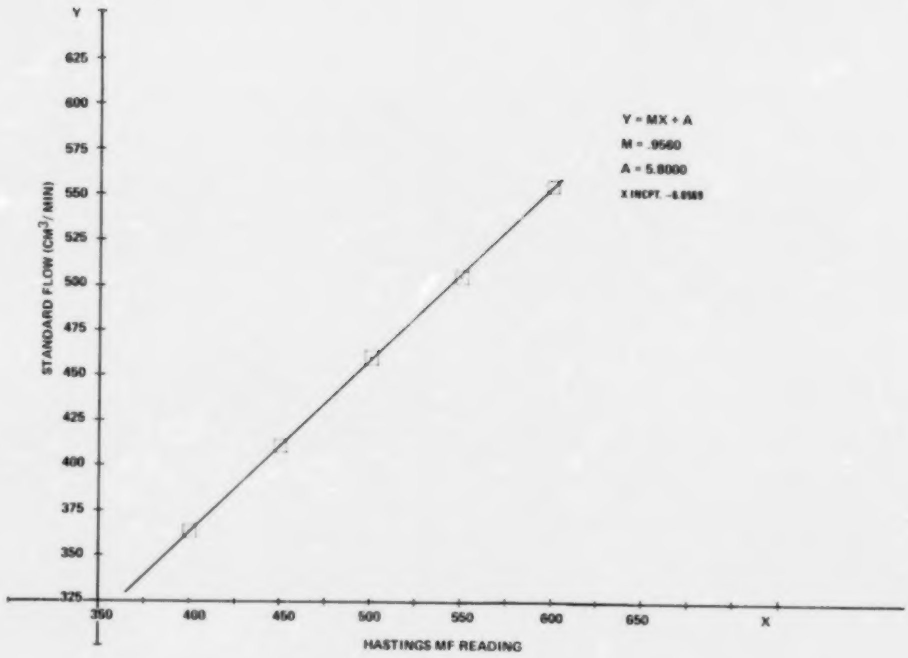

Figure 18. Hastings mass flowmeter calibration curve.

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familiar with the procedure by performing practice calibrations and applicable check-out procedures prior to their participation in the study.

Test Laboratory--After the initial set-up of the test laboratory reference system and equipment, appropriate calibration, certification, and check-out procedures were completed to ensure that the performance of the test system was suitable for the stated purpose of the study. These pre-test operations and pertinent test data are summarized in Appendix G.

Test Procedure--

Tests at Research Triangle Park, North Carolina--This phase of the study was designed so that 2 to 3 volunteers could simultaneously participate on a given test day. Volunteers were briefed on the test procedures and allowed sufficient time for set-up of equipment and any preliminary check-out operations. The test procedure for a typical test run is given below:

- Volunteer is given a set of chemicals from several commercial sources to be used for preparation of reagents.
- Volunteer prepares the required reagents.
- Volunteer prepares a calibration curve using his I_2 standards and spectrophotometer.
- Volunteer measures sample flow rate through his BAKI sampling train.
- Test coordinator measures sample flow rate using the reference Hastings mass flowmeter.
- Test coordinator generates an O_3 test concentration and continuously measures the test concentration with the reference system UV photometers.
- When the test concentration has stabilized, test coordinator instructs the volunteer to begin sampling the test concentration.
- Volunteer measures the test concentration using a 10-minute sampling period. Test coordinator simultaneously measures the test concentration using the reference system UV photometers. A second set of O_3 measurements (Volunteer and Reference) is then obtained at the same test concentration.
- Last 3 steps are repeated for each O_3 concentration level.

Duplicate measurements were thus obtained at five O_3 test concentrations (0.00, 0.40, 0.30, 0.20, 0.10 ppm). The complete procedure was then repeated starting with volunteer preparation of reagents using the same set of chemicals.

Tests at Field Locations--This phase of the study was conducted at three field locations (Frankfort, Kentucky; Albany, New York; Newbury Park, California). The two UV photometers used in the reference system for the tests at RTP were taken to the field locations. Because of the generally good agreement between the volunteer and reference flow measurements for the RTP tests and uncertainty about the reliability of the reference flow measurement device when transported to the field, reference flow measurements were not obtained at the field locations. The test procedure for this phase of the study is given below:

- Prior to arrival of the test coordinator, volunteer assembles BAKI calibration system, prepares the required reagents, and prepares calibration curve. On the day before the test coordinator's arrival, volunteer calibrates chemiluminescence O_3 analyzer.
- Test coordinator audits the calibrated chemiluminescence O_3 analyzer using one or both UV photometers. Required O_3 test concentrations are generated with the volunteer system and measured simultaneously with the volunteer calibrated O_3 analyzer and reference UV photometer(s).
- The second run is conducted in the same manner as the RTP tests except no reference flow measurement is obtained.

Data Analysis and Discussion of Results

Three of the RTP volunteers were asked to return for additional tests after their initial participation in the study. One of these volunteers used his own BAKI calibration apparatus and prepared the necessary reagents from a set of chemicals that had been used by an earlier volunteer.

Another of the volunteers used his own apparatus and the original set of chemicals except for the distilled water. The third of these volunteers used a different KI sampling train and the original set of chemicals except for the distilled water. Since each of these additional tests was conducted under experimental conditions somewhat different than during the volunteers' initial participation, they were treated as separate and not replicate runs. Therefore, the data analysis tabulates results for thirteen separate volunteers.

Ozone Calibrations by Boric Acid-Potassium Iodide--

Each of the volunteers measured two sets of O_3 atmospheres using his own BAKI calibration apparatus (for the three field volunteers, the first set of O_3 atmospheres was measured with a BAKI calibrated chemiluminescence O_3 analyzer). The O_3 concentrations were also measured simultaneously by the reference system UV photometers. The UV photometer readings were corrected for the temperature and pressure of the sample at the time of the measurement using Equation 6-5 below (the average of the two corrected UV photometer values was used as the reference O_3 measurement):

$$O_3\ (\text{Corr}) = O_3\ (\text{Ind}) \times \frac{45.682}{\text{Dasibi Span No.}} \times \frac{29.92}{P} \times \frac{T}{273.15} \qquad (6\text{-}5)$$

where:
O_3 (Corr) = corrected O_3 concentration, ppm
O_3 (Ind) = indicated O_3 concentration, ppm
45.682 = Dasibi span number at STP (0° C and 29.92 in Hg)
Dasibi Span No. = Dasibi span number during the O_3 measurements
29.92 = pressure at STP, in Hg
273.15 = temperature at STP, K
P = ambient pressure during O_3 measurement, in Hg
T = absorption cell temperature O_3 during measurement, K

A least squares linear regression equation was obtained for each set of O_3 atmospheres measured. Each regression equation was in the form of Equation 1-1. The regression constants are given in Table 36. The intercepts (B_2) of all the regression equations were examined statistically and were found not to be significantly different than zero.

An analysis of variance was performed on the regression slopes using the model of Equation 1-2. Results of the analysis of variance of the regression slopes are given in Table 37. The results of one of the RTP volunteers (volunteer 6) were discarded from the data set, based on the large difference in slopes from run 1 and 2. Therefore, Table 37 lists N = 12 volunteers for the total data and N = 9 volunteers for the data from tests conducted at RTP.

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The random component of variability ($\sigma_e = 0.0216$) for O_3 calibrations performed by the 12 volunteers (Table 37, Total BAKI) was about ± 2 percent of the mean slope. The calibration system component of variability ($\sigma_t = 0.0513$) was significant and amounted to approximately ± 5 percent of the mean slope. These results show that BAKI O_3 calibrations are dependent on the calibration system, which includes the operator, the equipment, and the reagents.

Reference flow measurements were obtained during each run performed by the RTP volunteers. Using these reference flow measurements, the O_3 (Volunteer) values and regression constants (Table 36) were recalculated. An analysis of variance was then performed on the uncorrected and corrected slopes for the RTP volunteers; the results indicated no significant difference in either the random (σ_e) or calibration system (σ_t) variability.

The BAKI (corrected) data in Table 37 represents RTP volunteer data with correction for the I_2 molar absorptivity applied. If the I_2 molar absorptivity was assumed to be 25,600 $l\ mole^{-1}\ cm^{-1}$ instead of being determined by each volunteer during the preparation of the calibration curve, the calibration system variability ($\sigma_t = 0.0415$) was slightly

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(4-76)

TABLE 36. REGRESSION CONSTANTS FOR BAKI O_3 CALIBRATION RUNS

Volunteer	Run	Slope (B_1)	Intercept (B_2)	S_{Int}	S_{Slope}	R^2
1	1	0.8665	0.0059	0.0045	0.0184	0.9964
	2	0.8941	0.0056	0.0069	0.0278	0.9923
2	1	0.9654	-0.0113	0.0043	0.0177	0.9973
	2	0.9863	0.0063	0.0046	0.0186	0.9972
3	1	1.0032	-0.0024	0.0021	0.0086	0.9994
	2	1.0189	-0.0032	0.0014	0.0058	0.9997
4	1	0.9893	-0.0086	0.0094	0.0384	0.9881
	2	1.0011	-0.0038	0.0035	0.0143	0.9984
5	1	0.8545	0.0029	0.0027	0.0108	0.9987
	2	0.9042	-0.0001	0.0024	0.0100	0.9990
6	1	1.1243	0.0273	0.0117	0.0431	0.9889
	2	0.9620	0.0070	0.0057	0.0231	0.9954
7	1	1.0060	0.0015	0.0015	0.0063	0.9997
	2	0.9977	0.0064	0.0043	0.0172	0.9976
8	1	1.0218	0.0024	0.0020	0.0079	0.9995
	2	0.9972	0.0074	0.0022	0.0089	0.9994
9	1	1.0118	-0.0089	0.0037	0.0149	0.9821
	2	0.9841	-0.0026	0.0013	0.0054	0.9756
10	1	1.0429	-0.0077	0.0056	0.0228	0.9962
	2	1.0396	-0.0029	0.0041	0.0166	0.9980
11	1	0.9926	-0.0006	0.0003	0.0012	1.0000
	2	1.0142	-0.0014	0.0016	0.0062	0.9997
12	1	1.0200	-0.0014	0.0008	0.0033	1.0000
	2	1.0492	-0.0097	0.0033	0.0128	0.9988
13	1	1.0446	-0.0045	0.0021	0.0081	0.9998
	2	1.0115	-0.0072	0.0035	0.0133	0.9983

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TABLE 37. VARIABILITY OF BAKI O_3 CALIBRATIONS

System	N*	Mean Slope	σ_e	σ_t	σ_{tot}**	Reproducibility
Total BAKI	12	0.9865	0.0216	0.0513	0.0557	0.1544
BAKI	9	0.9769	0.0175	0.0563	0.0590	0.1635
BAKI Corrected	9	0.9906	0.0177	0.0415	0.0451	0.1250

*N = number of participating volunteers

**$\sigma_{tot} = \sqrt{\sigma_e^2 + \sigma_t^2}$

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reduced. The last two lines of Table 37 compare uncorrected and corrected results for the volunteers who came to RTP. When corrections for reference flow measurements were applied to RTP volunteer data, no significant difference was observed.

The reproducibility (Equation 1-3) at the 95 percent level is given in the last column of Table 37. The difference between BAKI O_3 calibration slopes was less than 15.5 percent, 95 percent of the time. While individual calibration curves were dependent on the calibration system, the mean of the slopes for all BAKI O_3 calibrations was not significantly different than 1.000.

The analysis of variance for BAKI O_3 calibrations is summarized in Appendix I.

Summary of Conclusions from Variability Study of Boric Acid-Potassium Iodide Calibration Procedure

Reproducibility for BAKI calibrations employing the volunteer systems was $\leq$ 15.5 percent of the mean slope. When the molar absorptivity of I_2 was assumed to be 25,600 l^{-1} $mole^{-1}$ instead of it being determined during the calibration, the reproducibility was reduced to $\leq$ 12.5 percent of the mean slope.

Total variability can be broken into two parts: a random component (σ_e), and a calibration system component (σ_t). The random component of variability for O_3 calibrations using the volunteer BAKI systems was approximately ± 2 percent of the mean slope. The calibration system component of variability (± 5 percent of the mean slope) for O_3 calibrations using the volunteer BAKI systems was statistically significant and showed that the BAKI calibrations are subject to significant system dependent biases. Since no control system was used in the study, operator effects cannot be separated from equipment and reagent effects. However, the mean slope for O_3 calibrations using the volunteer BAKI systems showed no bias with respect to the UV photometric reference system.

With the large system dependent variability shown in this study, the BAKI procedure would be an unsatisfactory independent calibration procedure for reference methods for the determination of O_3 concentrations in the atmosphere.

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APPENDIX A

TENTATIVE CALIBRATION PROCEDURE USING ULTRAVIOLET PHOTOMETRY

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EPA-287 (Cin.)
(4-76)

APPENDIX A

TENTATIVE CALIBRATION PROCEDURE USING ULTRAVIOLET PHOTOMETRY

Major Equipment Required: Stable ozone generator, ultraviolet photometer

1. Principle.

1.1 The calibration procedure is based on the photometric measurement of ozone (O_3). The concentration of O_3 in an absorption cell is determined from a measurement of the amount of 254 nm light absorbed by the sample. This determination requires knowledge of the absorption coefficient (α) of O_3, the length (ℓ) of the optical path through the sample, and the transmittance (T) of the sample at 254 nm. The transmittance is defined as the ratio I/I_o, where I is the intensity of light which passes through the cell and reaches the detector when the cell contains a sample and I_o is the intensity of light which passes through the cell and reaches the detector when the cell is evacuated or contains some reference material. It is assumed that all conditions of the system, except for the contents of the absorption cell, are identical during measurement of I and I_o. The quantities defined above are related by the Beer-Lambert absorption law:

$$T = I/I_o = e^{-\alpha c \ell} \qquad (1)$$

where: $c = O_3$ concentration, ppm

The absorption coefficient of O_3 at 254 nm is approximately 3.10×10^{-4} ppm^{-1} cm^{-1}. (1,2,3,4,5)

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(4-76)

A stable O_3 generator is used to produce O_3 concentrations over the range required. Each O_3 concentration is determined by measuring T in a photometer of known pathlength, ℓ. The O_3 concentration is calculated from:

$$c = -\frac{1}{\alpha \ell} \ln T \qquad (2)$$

1.2 This procedure may be used either to calibrate an O_3 analyzer directly, or to calibrate a reproducible O_3 generator. When the procedure is used directly, the O_3 analyzer under calibration and the photometer are allowed to sample O_3 concentrations simultaneously. If the O_3 generator is calibrated prior to the O_3 analyzer, it must meet the requirements and specifications set forth in Reference 6, "Transfer Standards for Ozone Concentrations."

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2. Apparatus. Figure 1, a schematic of a typical dynamic calibration system, shows the suggested configuration of the components listed below. All connections between components in the calibration system between the O_3 generator and the photometer cell should be glass or Teflon®. Additional information regarding the assembly of a UV photometric calibration apparatus is given in Reference 7.

2.1 Air flow controllers. Devices capable of maintaining constant air flow within ± 2 percent.

2.2 Ozone generator. Device capable of generating stable levels of O_3 over the required concentration range.

2.3 Output manifold. The output manifold should be constructed of glass or Teflon®, and be of sufficient diameter to ensure a minimum pressure drop at the analyzer connection. The system must have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

2.4 Two-way valve. Manually actuated, air actuated, or solenoid valve of Teflon® construction.

2.5 Photometer. The photometer consists of a low-pressure mercury discharge lamp, collimation optics (optional), an absorption cell, a detector, and signal processing electronics. The length of the light path through the absorption cell must be known with an accuracy of at least 99.5 percent. The fractional error in the measurement of an O_3 concentration is related to the fractional error in the transmittance measurement by the expression:

$$\frac{dc}{c} = -\frac{dT}{T\ln T} \qquad (3)$$

The photometer must be constructed in such a fashion that the standard deviation of the transmittance measurement at a given O_3 concentration causes the standard deviation of the concentration measurement to be no more than 0.005 ppm or 3 percent of the concentration, whichever is the greater amount.

3. Reagents.

3.1 Zero Air. Air, free of contaminants which will cause a detectable response on the O_3 analyzer. The air should also be free of NO, C_2H_4, and other species which react with O_3. A procedure for generating zero air is given in Reference 7. When calibrating a transfer standard, zero air should be obtained from an ambient source, as other sources may vary in oxygen content, which would affect the accuracy of the transfer standard.

4. Procedure.

4.1 Assemble a dynamic calibration system such as shown in Figure 1.

EPA-287 (Cin.)
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4.2 Adjust the flowrate through the photometer absorption cell, F_P, to a convenient value so that the cell can be flushed in a reasonably short period of time (2 l/min is a typical flow). The time required for flushing is related to the precision of the measurement since photometer drift increases with time.

4.3 Adjust the flowrate through the O_3 generator, F_O, to a value at least 1 l/min greater than the total flowrate required by the photometer and the analyzer(s) under calibration.

4.4 Adjust the flowrate of zero air, F_Z, to a value at least 1 l/min greater than the flowrate required by the photometer.

4.5 Allow sufficient time for the O_3 analyzer and the photometer to warm-up and stabilize.

4.6 Allow the O_3 analyzer to sample zero air until a stable response is obtained and adjust the O_3 analyzer's zero control. Offsetting the analyzer's zero adjustment to + 5 percent of scale is recommended to facilitate observing negative zero drift. Record the stable zero air response as "Z".

4.7 Adjust the O_3 generator to produce an O_3 concentration of approximately 80 percent of the desired upper range limit (URL) of the O_3 analyzer.

4.8 Allow the O_3 analyzer to sample this O_3 concentration until a stable response is obtained. During the same time, actuate the two-way valve to allow the photometer to sample this O_3 concentration.

4.9 Record the temperature and pressure of the sample in the photometer absorption cell. (The photometer may be easily constructed in such a manner that the pressure of the sample is within a few tenths of a percent of ambient pressure. When using such a photometer the ambient

EPA-287 (Cin.)
(4-76)

atmospheric pressure provides a sufficiently accurate measurement of sample pressure.)

4.10 When the O_3 analyzer response has stabilized and the photometer absorption cell is thoroughly flushed, record the measured value of I.

4.11 Actuate the two-way valve to allow the photometer to sample zero air until the absorption cell is thoroughly flushed and record the measured value of I_o.

4.12 Calculate the O_3 concentration from:

$$[O_3]_{OUT} = \left(-\frac{1}{\alpha\ell}\right)\left(\ln\frac{I}{I_o}\right)\left(\frac{T}{273}\right)\left(\frac{760}{P}\right) \qquad (4)$$

where: $[O_3]_{OUT}$ = O_3 concentration, ppm

α = absorption coefficient of O_3 at 254 nm = 3.10×10^{-4} $ppm^{-1}cm^{-1}$

ℓ = optical pathlength, cm

T = sample temperature, °K

P = sample pressure, torr

4.13 Adjust the O_3 analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{OUT}}{URL} \times 100\right) + Z \qquad (5)$$

where: URL = upper range limit of the O_3 analyzer, ppm

Z = recorder response with zero air, % scale

Record the O_3 concentration and the analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating steps 4.6 and 4.13.

EPA-287 (Cin.)
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4.14 Generate several other O_3 concentrations (at least 5 others are recommended) over the scale range of the O_3 analyzer by adjusting the O_3 generator settings. Determine each O_3 concentration with the photometer using the procedure given above (steps 4.8 through 4.12). For each O_3 concentration, record the O_3 analyzer response and the corresponding O_3 analyzer concentration.

4.15 Plot the O_3 analyzer responses versus the corresponding O_3 concentrations and draw the O_3 analyzer's calibration curve or calculate the appropriate response factor.

4.16 OPTION 1: The various O_3 concentrations required in step 4.14 may be obtained by dilution of the O_3 concentration generated in step 4.7. With this option accurate flow measurements are required. The dynamic calibration system must be modified as shown in Figure 2 to allow for dilution air to be metered in downstream of the O_3 generator. A mixing chamber between the O_3 generator and the output manifold is also required. The flowrate through the O_3 generator (F_O) and the dilution air flowrate (F_D) are measured with a reliable standard traceable to NBS. Each O_3 concentration generated by dilution is calculated from:

$$[O_3]'_{OUT} = [O_3]_{OUT} \frac{(F_O)}{(F_O + F_D)} \tag{6}$$

where: $[O_3]'_{OUT}$ = diluted O_3 concentration, ppm
F_O = flowrate through the O_3 generator, scm^3/min
F_D = diluent air flowrate, scm^3/min

4.17 OPTION 2: An O_3 generator may be calibrated using the photometric procedure and then used as a transfer standard if it meets the requirements and specifications set forth in Reference 6. With this option, the O_3 generator output is calibrated at an accurately known flowrate through the O_3 generator (F_O). The O_3 generator is subsequently used with this same flowrate to calibrate the O_3 analyzer. Since the O_3 output of the generator is dependent on the oxygen content of the zero air, the

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oxygen content in the zero air during calibration of the generator must be the same as in the zero air used during calibration of the O_3 analyzer. Purified ambient air is recommended and a procedure for zero air generation is given in Reference 7.

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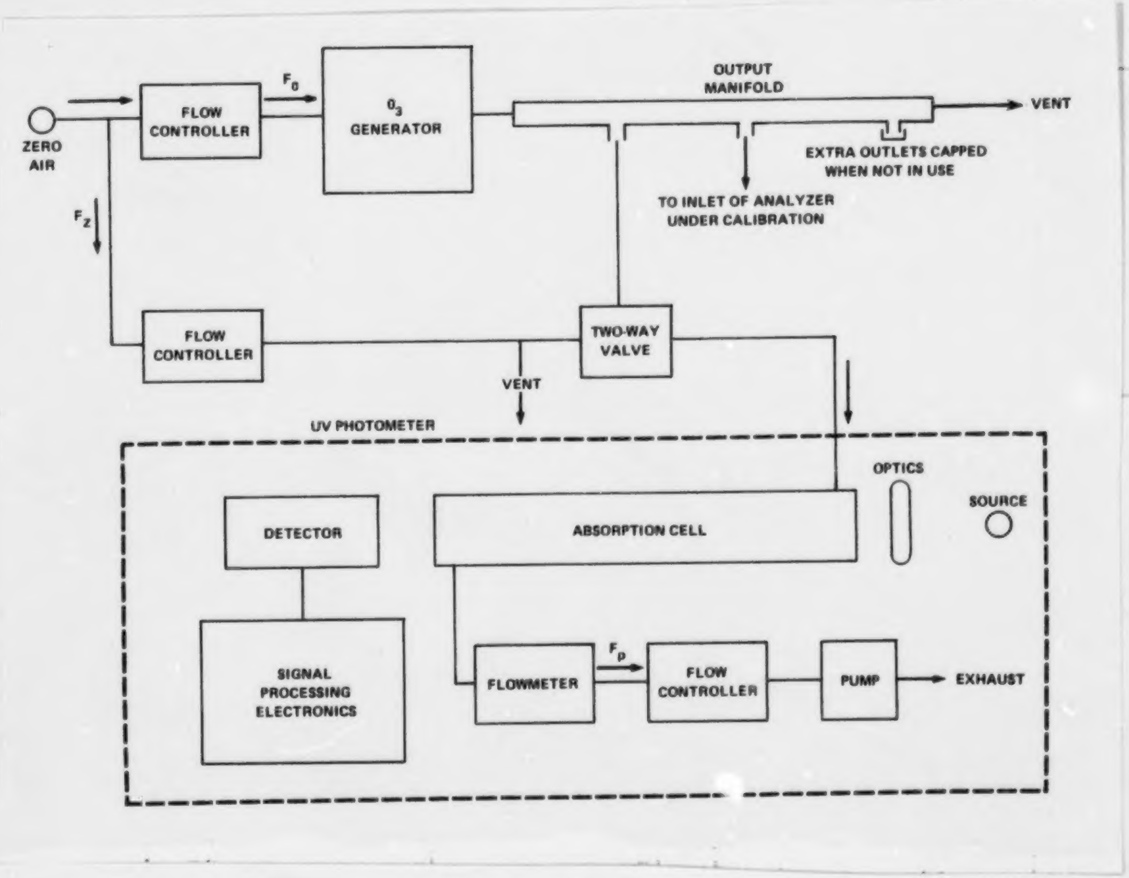
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Figure 1. Schematic diagram of a typical UV photometric calibration system.

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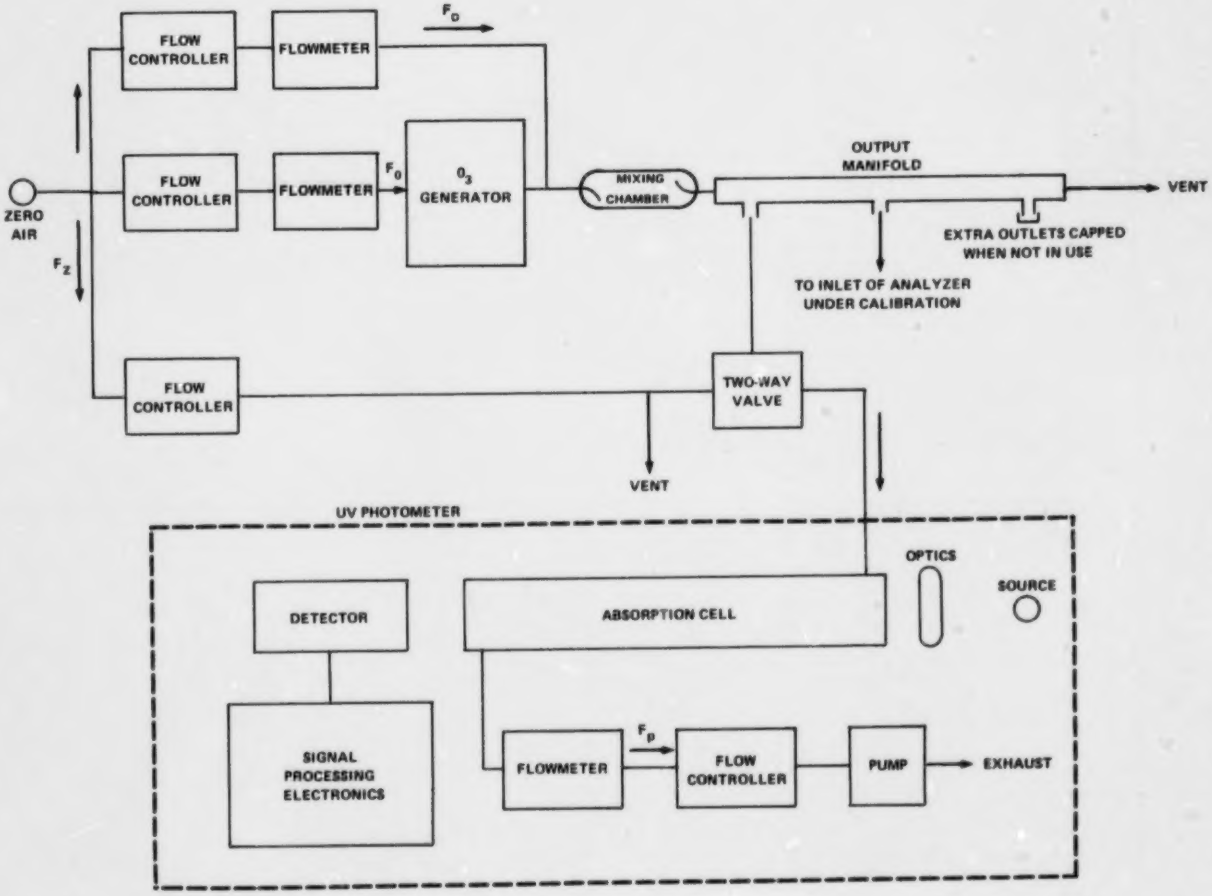
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Figure 2. Schematic diagram of a typical UV photometric calibration system (Option 1).

EPA-287 (Cin.)
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APPENDIX B

TENTATIVE CALIBRATION PROCEDURE USING GAS PHASE TITRATION WITH EXCESS NITRIC OXIDE

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

APPENDIX B

TENTATIVE CALIBRATION PROCEDURE USING GAS PHASE TITRATION WITH EXCESS NITRIC OXIDE

Major Equipment Required: Stable ozone generator, chemiluminescence NO analyzer with strip chart recorder, NO concentration standard

1. Principle.

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1.1 The calibration procedure is based upon the rapid gas phase reaction between nitric oxide (NO) and ozone (O_3) as described by the following equation:(1)

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$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

When O_3 is added to excess NO in a dynamic system, the decrease in NO concentration is equal to the concentration of O_3 added. The NO is obtained from a standard NO cylinder and O_3 is produced by a stable O_3 generator. A chemiluminescence NO analyzer is used to measure the change in NO concentration. The concentration of O_3 added may be varied to obtain calibration concentrations over the range desired. The dynamic system is designed to produce locally high concentrations of NO and O_3 in the reaction chamber, with subsequent dilution, to ensure complete O_3 reaction with relatively small chamber volumes.

1.2 This procedure may be used either to calibrate an O_3 analyzer directly, or (more commonly) to calibrate an O_3 generator. In the latter case, the O_3 generator is normally used immediately after calibration and without physical movement, and is recalibrated prior to each use. If the O_3 generator is to be used at other times without recalibration or at other locations as a transfer standard, it must meet the requirements and

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(4-76)

specifications set forth in Reference 2, "Transfer Standards for Ozone Concentrations."

1.3 When this procedure is used directly to calibrate an O_3 analyzer, the O_3 concentration is first established by gas phase titration (GPT), then the NO flow is diverted to allow the O_3 concentration to pass to the output manifold.

2. Apparatus. Figure 1, a schematic of a typical GPT apparatus, shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream from the O_3 generator should be glass or Teflon®. Additional information regarding the assembly of a GPT calibration apparatus is given in Reference 3.

2.1 Air flow controllers. Devices capable of maintaining constant air flow within ± 2 percent.

2.2 Nitric oxide flow controller. A device capable of maintaining constant NO flow within ± 2 percent. Component parts in contact with the NO must be of a non-reactive material.

2.3 Air flowmeters. Properly calibrated flowmeters capable of measuring and monitoring air flows within ± 2 percent.

2.4 Nitric oxide flowmeter. A properly calibrated flowmeter capable of measuring and monitoring NO flows within ± 2 percent. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

2.5 Pressure regulator for standard NO cylinder. This regulator must have non-reactive internal parts and a suitable delivery pressure.

2.6 Ozone generator. Capable of generating stable levels of O_3 over the range and flow rates required (see Step 4 below).

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EPA-287 (Cin.)
(4-76)

2.7 Reaction chamber. A glass chamber for the quantitative reaction of O_3 with excess NO. The chamber should be of sufficient volume (V_{RC}) such that the residence time (t_R) is as specified in Step 4. For practical reasons, t_R should be less than 2 minutes.

2.8 Mixing chamber. A glass chamber of proper design to provide thorough mixing of reaction products and diluent air. The residence time is not critical when the dynamic parameter specifications given in Step 4 are met.

2.9 Output manifold. The output manifold should be constructed of glass or Teflon® of sufficient diameter to ensure a minimum pressure drop at the analyzer connection. The system must have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

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2.10 Chemiluminescence NO analyzer. The NO channel of a chemiluminescence $NO/NO_2/NO_x$ analyzer which essentially meets the (proposed) performance requirements for reference and equivalent methods for NO_2 (Federal Register 41:11264, March 17, 1976), may be used.

3. Reagents.

3.1 Nitric oxide concentration standard. Cylinder containing 50 to 100 ppm NO in N_2. This standard must be traceable to a National Bureau of Standards (NBS) NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684) or NO_2 Standard Reference Material (SRM 1629). The cylinder (working standard) should be recertified on a regular basis as determined by the local quality control program. (See Reference 3.)

3.2 Zero air. The air must be free of contaminants which will cause a detectable response on the NO or O_3 analyzer or which might react with either NO or O_3 in the GPT. A procedure for generating zero air is given in Reference 3. When calibrating a transfer standard, zero air should be

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

obtained from an ambient air source, as other sources of air may vary in oxygen content, which would affect the accuracy of the transfer standard.

4. Dynamic parameter specifications.

4.1 The residence time (t_R) in the reaction chamber and the gas flows (F_O and F_{NO}) (see Figure 1) must be adjusted according to the following relationships:

$$P_R = [NO]_{RC} \times t_R \geq 3.75 \text{ ppm-min} \qquad (2)$$

$$[NO]_{RC} = [NO]_{STD} \left(\frac{F_{NO}}{F_O + F_{NO}} \right) \qquad (3)$$

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} < 2 \text{ min} \qquad (4)$$

where:
P_R = dynamic specification, determined empirically, to ensure complete reaction of the available O_3, ppm-min
$[NO]_{RC}$ = NO concentration in the reaction chamber, ppm
t_R = residence time in the reaction chamber, min
$[NO]_{STD}$ = concentration of the undiluted NO standard, ppm
F_{NO} = NO flow, scm^3/min
F_O = O_3 generator air flow, scm^3/min
V_{RC} = volume of the reaction chamber, scm^3

4.2 These parameters may be selected according to the following sequence:

4.2.1 Determine F_T, the total flow required at the output manifold (F_T = analyzer(s) demand plus 10 to 50 percent excess).

4.2.2 Establish $[NO]_{OUT}$ as the highest NO concentration (ppm) which will be required at the output manifold. $[NO]_{OUT}$ should be approximately

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PAGE
EPA-287 (Cin.)
(4-76)

equivalent to 90 percent of the upper range limit (URL) of the O_3 concentration range to be covered.

4.2.3 Determine F_{NO} as:

$$F_{NO} = \frac{[NO]_{OUT} \times F_T}{[NO]_{STD}} \qquad (5)$$

4.2.4 Select a convenient or available reaction chamber volume. Initially, a trial V_{RC} may be selected to be in the range of approximately 200 to 500 scm^3.

4.2.5 Compute F_O as:

$$F_O = \sqrt{\frac{[NO]_{STD} \times F_{NO} \times V_{RC}}{3.75}} - F_{NO} \qquad (6)$$

4.2.6 Compute t_R as:

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} \qquad (7)$$

Verify that $t_R < 2$ minutes. If not, select a reaction chamber with a smaller V_{RC}.

4.2.7 Compute F_D as:

$$F_D = F_T - F_O - F_{NO} \qquad (8)$$

where: F_D = diluent air flow, scm^3/min

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EPA-287 (Cin.)
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4.2.8 If F_0 turns out to be impractical for the desired system, select a reaction chamber having a different V_{RC} and recompute F_0 and F_D. For a more detailed discussion of these requirements and other related considerations as well as example calculations, refer to Reference 3.

5. Procedure.

5.1 Assemble a dynamic calibration system such as shown in Figure 1.

5.2 Establish the dynamic parameters as indicated in Step 4.

5.3 Ensure that all flowmeters are properly calibrated under the conditions of use against a reliable standard such as a soap-bubble meter or wet-test meter traceable to NBS. All volumetric flowrates should be corrected to 25° C and 760 torr. A detailed discussion on proper calibration of flowmeters is given in Reference 3.

5.4 Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by: (1) carefully evacuating the regulator, when possible, after the regulator has been connected to the cylinder and before opening the cylinder valve; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; and, (3) not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in Reference 3.

5.5 Adjust the diluent air and O_3 generator air flows to obtain the flows determined in Step 4.2. The total air flow must exceed the total demand of the analyzer(s) connected to the output manifold to ensure that no ambient air is pulled into the manifold vent.

5.6 Calibration of the NO analyzer.

5.6.1 Allow sufficient time for the NO analyzer to warm-up and stabilize.

5.6.2 Allow the NO analyzer to sample zero air until a stable NO response is obtained, and make the proper zero adjustments.

5.6.3 Adjust F_{NO} to obtain an NO output concentration of approximately 80 percent of the upper range limit (URL) of the NO range. The exact concentration is calculated from:

$$[NO]_{OUT} = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D} \qquad (9)$$

where: $[NO]_{OUT}$ = diluted NO concentration at the output manifold, ppm

Sample this NO concentration until the NO analyzer response has stabilized. Adjust the NO span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \frac{[NO]_{OUT}}{URL} \times 100 \qquad (10)$$

where: URL = upper range limit of the NO analyzer, ppm

Record the NO concentration and the analyzer response. The NO analyzer should be spanned to the same range as that of the O_3 analyzer to be calibrated. If substantial adjustment of the span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating Steps 5.6.2 and 5.6.3.

5.6.4 Generate several additional NO concentrations (at least five are suggested to verify linearity) by decreasing F_{NO} or increasing F_D. For each NO concentration, calculate the exact NO concentration generated using Equation 9 and record the analyzer response. Plot the analyzer

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response versus the calculated NO concentration and draw the NO calibration curve. This plot should be linear. For subsequent calibrations, this curve may be verified with a two-point calibration.

5.7 Calibration of the ozone generator.

5.7.1 Adjust F_O, F_{NO}, and F_D as determined in Step 4.2 and generate an NO concentration near 90 percent of the URL of the NO range. Using the NO analyzer and calibration curve obtained in Step 5.6.4, measure and record this NO concentration as $[NO]_{orig}$.

5.7.2 Adjust the O_3 generator to generate sufficient O_3 to produce a decrease in NO concentration equivalent to approximately 80 percent of the URL. The O_3 concentration must not exceed 90 percent of the available NO concentration.

5.7.3 Calculate the corresponding O_3 concentration as:

$$[O_3]_{OUT} = ([NO]_{orig} - [NO]_{rem}) \frac{(F_O + F_{NO} + F_D)}{(F_O + F_D)} \qquad (11)$$

where: $[O_3]_{OUT}$ = O_3 concentration at the output manifold when $F_{NO} = 0$, ppm
$[NO]_{orig}$ = original NO concentration, ppm
$[NO]_{rem}$ = NO concentration remaining after addition of O_3, ppm

Record this O_3 concentration and the corresponding generator settings.

5.7.4 Adjust the O_3 generator settings to obtain other O_3 concentrations over the desired range, using Equation 11 to calculate the corresponding O_3 concentration (five or more calibration points are recommended). Plot the O_3 concentration versus the generator settings and draw the O_3 generator calibration curve.

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EPA-287 (Cin.)
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5.8 Calibration of the ozone analyzer.

5.8.1 Allow sufficient time for the O_3 analyzer to warm-up and stabilize.

5.8.2 Allow the O_3 analyzer to sample zero air until a stable response is obtained and adjust the O_3 analyzer's zero control. Offsetting the analyzer's zero adjustment to + 5 percent of scale is recommended to facilitiate observing negative zero drift. Record the stable zero air response as "Z".

5.8.3 Using the O_3 generator as calibrated above, and the same F_O and F_D, generate an O_3 concentration near 80 percent of the desired URL of the analyzer.

5.8.4 Allow the O_3 analyzer to sample this O_3 concentration until a stable response is obtained. Adjust the analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{OUT}}{URL} \times 100\right) + Z \qquad (12)$$

where: URL = upper range limit of the O_3 analyzer, ppm
Z = recorder response with zero air, % scale

Record the O_3 concentration and the analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating Steps 5.8.2 and 5.8.4.

5.8.5 Generate several other O_3 concentrations (at least five others are recommended) over the scale range of the analyzer by adjusting the O_3 generator settings (preferably the same settings as used in Step 5.7.4). For each O_3 concentration, allow for a stable analyzer response, then record the response and the corresponding O_3 concentration.

5.8.6 Plot the O_3 analyzer responses versus the corresponding O_3 concentrations and draw the O_3 analyzer's calibration curve or calculate the appropriate response factor.

5.8.7 OPTION 1: The various O_3 concentrations required in Step 5.8.5 may be obtained by dilution of the O_3 concentration generated in Step 5.8.3. In this case, F_D is increased to various values to decrease the O_3 output concentration, which is calculated as:

$$[O_3]'_{OUT} = [O_3]_{OUT} \frac{(F_O + F_D)}{(F_O + F'_D)} \qquad (13)$$

where: F'_D = the new diluent air flow, scm^3/min

Since only one O_3 generator setting is used, the generator need be calibrated only at this setting, or $[O_3]_{OUT}$ may be calculated from Equation 11 without actually calibrating the O_3 generator if the setting is not changed from that used in Steps 5.7.2 and 5.7.3.

5.8.8 OPTION 2: The O_3 analyzer may be calibrated "directly" by GPT without intermediate calibration of the O_3 generator and without changing F_D. Under this option, the various O_3 concentrations required for calibration in Steps 5.8.4 and 5.8.5 are obtained by adjusting the O_3 generator settings. For each such adjustment, the O_3 concentration is first established by GPT using Equation 11. Then the NO flow is diverted to allow the O_3 to be delivered to the output manifold and sampled by the analyzer.

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2. Transfer Standards for Ozone Concentrations. EPA Publication (to be prepared).

3. Technical Assistance Document for the Chemiluminescence Measurement of Ozone. EPA Publication (to be prepared).

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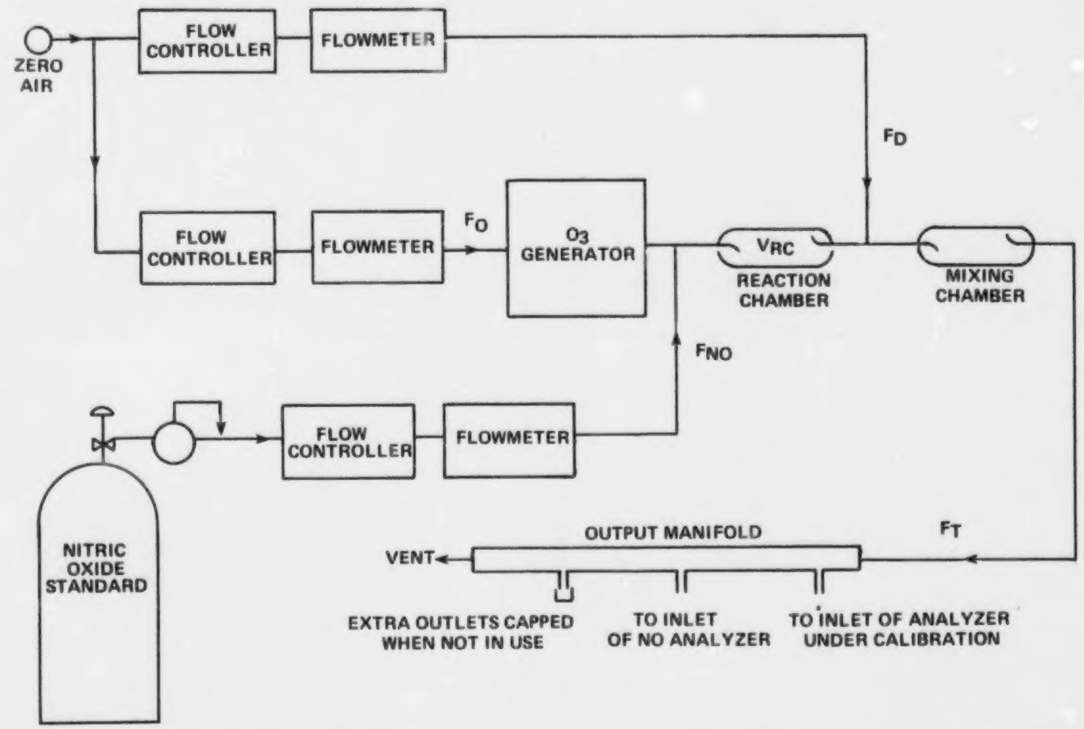
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Figure 1. Schematic diagram of a typical GPT calibration system.

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APPENDIX C

TENTATIVE CALIBRATION PROCEDURE USING GAS PHASE TITRATION WITH EXCESS OZONE

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EPA-287 (Cin.)
(4-76)

APPENDIX C

TENTATIVE CALIBRATION PROCEDURE USING GAS PHASE TITRATION WITH EXCESS OZONE

Major Equipment Required: Stable ozone generator, NO concentration standard

1. Principle.

1.1 The calibration procedure is based upon the rapid gas phase reaction between ozone (O_3) and nitric oxide (NO) in accordance with the following equation:[1]

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

The quantitative nature of this reaction is such that the amounts of NO and O_3 reacted are equivalent. Nitric oxide is added to O_3 in a dynamic system, and the chemiluminescence O_3 analyzer under calibration is used as an indicator of changes in O_3 concentration. The decrease in O_3 response observed on the uncalibrated O_3 analyzer is equivalent to the concentration of NO added. By measuring this decrease in response and the initial response, the O_3 concentration can be determined. Additional O_3 calibration concentrations are generated by a dilution technique. The dynamic system is designed to produce locally high concentrations of O_3 and NO in the reaction chamber, with subsequent dilution, to ensure complete NO reaction with relatively small chamber volumes.

2. Apparatus. Figure 1, a schematic of a typical GPT apparatus, shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream from the O_3 generator should be glass or Teflon®. Additional information regarding the assembly of a GPT calibration apparatus is given in Reference 2.

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2.1 Air flow controllers. Devices capable of maintaining constant air flow within ± 2 percent.

2.2 Nitric oxide flow controller. A device capable of maintaining constant NO flow within ± 2 percent. Component parts in contact with the NO must be of a non-reactive material.

2.3 Air flowmeters. Properly calibrated flowmeters capable of measuring and monitoring air flows within ± 2 percent.

2.4 Nitric oxide flowmeter. A properly calibrated flowmeter capable of measuring and monitoring NO flows within ± 2 percent. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

2.5 Pressure regulator for standard NO cylinder. This regulator must have non-reactive internal parts and a suitable delivery pressure.

2.6 Ozone generator. Capable of generating a stable level of O_3 at the flow rates required (see Step 4 below).

2.7 Reaction chamber. A glass chamber for the quantitative reaction of NO with excess O_3. The chamber should be of sufficient volume (V_{RC}) such that the residence time (t_R) is as specified in Step 4.

2.8 Mixing chamber. A glass chamber of proper design to provide thorough mixing of reaction products and diluent air. The residence time is not critical when the dynamic parameter specifications given in Step 4 are met.

2.9 Output manifold. The output manifold should be constructed of glass or Teflon® of sufficient diameter to ensure a minimum pressure drop at the analyzer connection. The system must have a vent designed to ensure

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atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

3. Reagents.

3.1 Nitric oxide concentration standard. Cylinder containing 50 to 100 ppm NO in N_2. The cylinder must be traceable to a National Bureau of Standards (NBS) NO in N_2 Standard Reference Material (SRM 1683 or SRM 1684) or NO_2 Standard Reference Material (SRM 1629). The cylinder (working standard) should be recertified on a regular basis as determined by the local quality control program (Reference 2).

3.2 Zero Air. The air must be free of contaminants which will cause a detectable response on the O_3 analyzer or which might react with either NO or O_3 in the gas phase titration. A procedure for generating zero air is given in Reference 2.

4. Dynamic parameter specifications.

4.1 The residence time (t_R) in the reaction chamber and the gas flows (F_O and F_{NO}) (Figure 1) must be adjusted according to the following relationships:

$$P_R = [O_3]_{RC} \times t_R = 1.5 \text{ ppm-min} \qquad (2)$$

$$[O_3]_{RC} = [O_3]_{OUT}\left(\frac{F_T}{F_O + F_{NO}}\right) \qquad (3)$$

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} \qquad (4)$$

where: P_R = dynamic specification, determined empirically, to ensure complete reaction of NO, ppm-min

$[O_3]_{RC}$ = O_3 concentration in the reaction chamber, ppm

t_R = residence time in the reaction chamber, min
$[O_3]_{OUT}$ = 80 percent (URL) concentration of O_3 at the output manifold, ppm
F_T = total flow at the output manifold, scm^3/min
F_O = O_3 generator air flow, scm^3/min
F_{NO} = NO flow, scm^3/min
V_{RC} = volume of the reaction chamber, scm^3

4.2 These parameters may be selected according to the following sequence:

4.2.1 Determine F_T, the total flow required at the output manifold (F_T = analyzer(s) demand plus 10 to 50 percent excess).

4.2.2 Determine $[O_3]_{OUT}$ as the 80 percent URL concentration required at the output manifold.

4.2.3 Determine F_{NO} as:

$$F_{NO} = \frac{0.8 \times [O_3]_{OUT} \times F_T}{[NO]_{STD}} \qquad (5)$$

where: $[NO]_{STD}$ = concentration of the undiluted NO standard, ppm

4.2.4 Select a convenient or available reaction chamber volume. Initially, a trial V_{RC} may be selected to be in the range of approximately 300 to 1500 scm^3.

4.2.5 Compute F_O as:

$$F_O = \sqrt{\frac{[O_3]_{OUT} \times F_T \times V_{RC}}{1.5}} - F_{NO} \qquad (6)$$

EPA-287 (Cin.)
(4-76)

4.2.6 Compute t_R as:

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} \qquad (7)$$

4.2.7 Compute F_D as:

$$F_D = F_T - F_O - F_{NO} \qquad (8)$$

where: F_D = diluent air flow, scm^3/min

4.2.8 If F_O turns out to be impractical for the desired system, select a reaction chamber having a different V_{RC} and recompute F_O and F_D. For a more detailed discussion of these requirements and other related considerations as well as example calculations, refer to Reference 2. A procedure for the initial checkout of the GPT system and the dynamic parameter specifications given above is also included in Reference 2.

5. Procedure.

5.1 Assemble a dynamic calibration system such as shown in Figure 1.

5.2 Establish the dynamic parameters as indicated in Step 4.

5.3 Ensure that all flowmeters are properly calibrated under the conditions of use against a reliable standard such as a soap-bubble meter or wet-test meter traceable to NBS. All volumetric flowrates should be corrected to 25° C and 760 torr. A detailed discussion on proper calibration of flowmeters is given in Reference 2.

5.4 Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by (1) carefully evacuating the regulator, when possible, after

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(4-76)

the regulator has been connected to the cylinder and before opening the cylinder valve; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; and, (3) not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in Reference 2.

5.5 Allow sufficient time for the O_3 analyzer to warm-up and stabilize. Adjust the diluent air and O_3 generator air flows to obtain the flows determined in Step 4.2. The total air flow must exceed the demand of the analyzer under calibration to ensure that no ambient air is pulled into the manifold vent. Allow the O_3 analyzer to sample zero air until a stable response is obtained and adjust the analyzer's zero control. Offsetting the analyzer's zero adjustment to + 5 percent of scale is recommended to facilitate observing negative zero drift. Record the stable zero air response as "Z".

5.6 Adjust the O_3 generator to generate an O_3 concentration of approximately 80 percent of the URL as measured on the uncalibrated O_3 analyzer. When the response has stabilized, record as I_o (corrected for zero offset, Z).

5.7 Turn the NO flow on and adjust until the O_3 analyzer response has been decreased by 75 to 80 percent of its original value. For example, if I_o = 80 percent of the URL, the NO flow should be adjusted to give a resultant analyzer response of 16 to 20 percent of the URL. When the resultant response has stabilized, record as I (corrected for zero offset, Z).

5.8 Measure the NO flow and record as F_{NO}.

5.9 Calculate the exact NO concentration from:

$$[NO] = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D} \qquad (9)$$

where: [NO] = diluted NO concentration, ppm

EPA-287 (Cin.)
(4-76)

5.10 Calculate the O_3 concentration from:

$$[O_3]_{OUT} = \frac{I_o}{I_o \times \frac{F_O + F_D}{F_{NO} + F_O + F_D} - I} \times [NO] \qquad (10)$$

$$\sim \frac{I_o}{I_o - I} \times [NO] \qquad (11)$$

where: $[O_3]_{OUT}$ = O_3 concentration, ppm
I_o = original O_3 analyzer response, percent chart (corrected for zero offset, Z)
I = resultant O_3 analyzer response after addition of NO, percent chart (corrected for zero offset, Z)

(The correction for flow dilution by NO shown in Equation 10 is usually small and may be ignored by using Equation 11.)

5.11 Remove the NO flow. The O_3 analyzer response should return to its original value.

5.12 Adjust the analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{OUT}}{URL} \times 100\right) + Z \qquad (12)$$

where: URL = upper range limit of the O_3 analyzer, ppm
Z = recorder response with zero air, percent scale

Record the O_3 concentration and the analyzer response. If substantial adjustment of the span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating Steps 5.5 and 5.12. If the O_3 concentration calculated above is outside the desired range of the analyzer, span the analyzer on the next higher range and then repeat the entire

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

procedure (Steps 5.5 through 5.12) on the desired range.

5.13 Calculate the O_3 concentration produced by the O_3 generator from:

$$[O_3]_{GEN} = [O_3]_{OUT} \frac{(F_O + F_D)}{(F_O)} \tag{13}$$

where: $[O_3]_{GEN}$ = O_3 concentration produced by the O_3 generator, ppm

5.14 Generate several other O_3 concentrations (at least four are suggested) by increasing F_D, the diluent air flow. Calculate the diluted O_3 concentrations from:

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$$[O_3]'_{OUT} = [O_3]_{GEN} \frac{(\quad F_O \quad)}{(F_O + F'_D)} \tag{14}$$

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where $[O_3]'_{OUT}$ = diluted O_3 concentration, ppm

F_D' = the new diluent air flow, scm^3/min

5.15 Allow the O_3 analyzer to sample each diluted O_3 concentration until a stable response is obtained. For each concentration, record the analyzer response and the corresponding O_3 concentration.

5.16 Plot the O_3 analyzer responses versus the corresponding O_3 concentrations and draw the O_3 analyzer's calibration curve or calculate the appropriate response factor.

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EPA-287 (Cin.)
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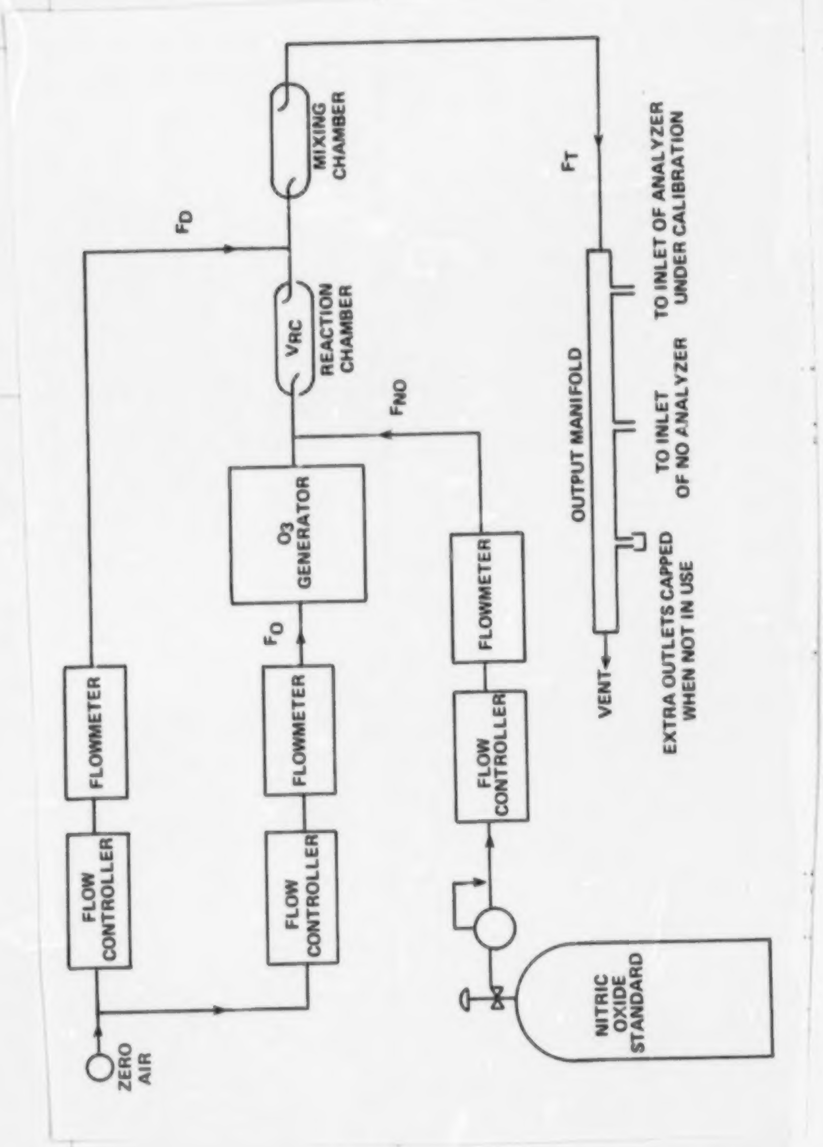
EPA-287 (Cin.)
(4-76)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MIXING CHAMBER
F_{NO}
NITRIC OXIDE STANDARD
FLOW CONTROLLER
FLOWMETER
VENT
OUTPUT MANIFOLD
F_T
EXTRA OUTLETS CAPPED WHEN NOT IN USE
TO INLET OF NO ANALYZER
TO INLET OF ANALYZER UNDER CALIBRATION

Figure 1. Schematic diagram of a typical GPT calibration system.

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

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APPENDIX D

TENTATIVE CALIBRATION PROCEDURE USING BORIC ACID-POTASSIUM IODIDE (BAKI)

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

APPENDIX D

TENTATIVE CALIBRATION PROCEDURE USING BORIC ACID-POTASSIUM IODIDE (BAKI)

Major Equipment Required: Stable ozone generator, spectrophotometer

1. Principle.

1.1 The calibration procedure is based upon the reaction between ozone (O_3) and potassium iodide (KI) with a stoichiometry as indicated in the classical equation:(1)

$$O_3 + 2H^+ + 2I^- \rightarrow O_2 + I_2 + H_2O \qquad (1)$$

The stoichiometry is such that the amounts of O_3 absorbed and iodine (I_2) released are equivalent. Ozone is absorbed in a 0.1 M boric acid (H_3BO_3) solution containing 1 percent KI and the I_2 released is measured spectrophotometrically at 352 nm. The output of a stable O_3 generator is determined in this manner and the generator is subsequently used to calibrate the chemiluminescence O_3 analyzer. The O_3 generator is normally used immediately after calibration and without physical movement, and is recalibrated prior to each use. If the O_3 generator is to be used at other times without recalibration or at other locations as a transfer standard, it must meet the requirements and specifications set forth in Reference 2, "Transfer Standards for Ozone Concentrations."

2. Apparatus.

2.1 Air flow controller. Device capable of maintaining constant air flow through the O_3 generator within ± 2 percent.

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EPA-287 (Cin.)
(4-76)

2.2 Air flowmeter. Calibrated flowmeter capable of measuring and monitoring air flow through the O_3 generator within ± 2 percent.

2.3 Ozone generator. Device capable of generating stable levels of O_3 over the required concentration range.

2.4 Output manifold. The output manifold should be constructed of glass or Teflon® of sufficient diameter to ensure a minimum pressure drop at the analyzer connection. The system must have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

2.5 Impingers. All glass impingers with the specifications indicated in Figure 2 are recommended. The impingers may be purchased from most major glassware suppliers. Two absorbers in series are needed to ensure complete collection of the sample.

2.6 Air pump and flow controller. Any pump and flow control device capable of maintaining a constant flow of 0.4 - 0.6 l/min through the impingers may be used. A critical orifice as described by Lodge (3) is recommended. The orifice should be protected against particulate matter with a membrane filter. The air pump should be capable of maintaining a pressure differential of 0.6 - 0.7 atmospheres across the critical orifice. Alternatively, a needle valve could be used with the pump to control the flow through the impingers. A flowmeter is then recommended to monitor the flow and the needle valve-flowmeter combination should be protected by means of a glass wool or drierite trap.

2.7 Thermometer. With an accuracy of ± 0.2° C.

2.8 Barometer. Accurate to the nearest mm Hg.

2.9 Volumetric flasks. 25, 100, 500, 1000-ml.

2.10 Buret. 50-ml.

2.11 Pipets. 1, 2, 3, 4, 5, 10, 20, 25, and 50-ml volumetric.

2.12 Erlenmeyer flasks. 300-ml.

2.13 Spectrophotometer. Capable of measuring absorbance at 352 nm. Matched 1-cm cells should be used.

3. Reagents.

3.1 Zero air. The air must be free of contaminants which will cause a detectable response on the O_3 analyzer, or which might react with 1 percent BAKI. Air meeting this requirement is obtained by passing it through silica gel for drying, treating with ozone to convert any NO to NO_2, and finally by passing through activated charcoal (6-14 mesh) and molecular sieve (6-16 mesh, type 4A) to remove any NO_2, hydrocarbons and traces of water vapor. When calibrating a transfer standard, zero air should be obtained from an ambient air source, as other sources of air may vary in oxygen content, which would affect the accuracy of the transfer standard.

3.2 Purified water. Distilled or deionized. Used for all reagents.

3.3 Absorbing reagent. Dissolve 6.2 g boric acid (H_3BO_3) and 10.0 g potassium iodide (KI) in purified water and dilute to 1000 ml. The pH should be 4.8 ± 0.2.

3.4 Standard arsenious oxide solution (0.05 N). Use primary standard grade arsenic trioxide (As_2O_3). Dry 1 hour at 105° C immediately before using. Accurately weigh 2.47 g arsenic trioxide from a small glass-stoppered weighing bottle. Dissolve in 25 ml 1 N sodium hydroxide in a flask or beaker on a steam bath. NOTE: Be sure all of the arsenic trioxide is dissolved. Add 25 ml 1 N sulfuric acid. Cool, transfer

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PAGE NUMBER

EPA-287 (Cin.)
(4-76)

quantitatively to a 1000-ml volumetric flask, and dilute to volume. NOTE: Solution must be neutral to litmus, not alkaline. Calculate the As_2O_3 normality as:

$$\text{Normality } As_2O_3 = \frac{\text{wt } As_2O_3\text{(g)}}{49.46} \tag{2}$$

3.5 Starch indicator solution (0.2 percent). Triturate 0.4 g soluble starch and approximately 2 mg mercuric iodide (preservative) with a little water. Add the paste slowly to 200 ml of boiling water. Continue boiling until the solution is clear, allow to cool, and transfer to a glass-stoppered bottle.

5-1/2"

3.6 Standard potassium iodate solution (0.1 N). Use primary standard grade potassium iodate (KIO_3). Dry 1 hour at 180° C immediately before using. Accurately weigh 3.57 g potassium iodate from a small glass-stoppered weighing bottle. Dissolve in purified water and dilute to 1000 ml. Calculate the KIO_3 normality as:

$$\text{Normality } KIO_3 = \frac{\text{wt } KIO_3\text{(g)}}{35.67} \tag{3}$$

3.7 Standard iodine solution (0.05 N).

3.7.1 Method A. Dissolve 5.0 g potassium iodide (KI) and 3.2 g resublimed iodine (I_2) in 10 ml purified water. When the iodine dissolves, transfer the solution to a 500-ml glass-stoppered volumetric flask. Dilute to mark with purified water and mix thoroughly. Keep solution in a dark brown glass-stoppered bottle away from light, and standardize as necessary. To standardize, pipet accurately 20 ml standard arsenious oxide solution into a 300-ml Erlenmeyer flask. Acidify slightly with 1:10 sulfuric acid, neutralize with solid sodium bicarbonate, and add about 2 g excess. Titrate with iodine solution using 5 ml starch solution as indicator. Saturate the solution with carbon dioxide near the end point by adding 1 ml

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EPA-287 (Cin.)
(4-76)

of 1:10 sulfuric acid. Continue the titration to the first appearance of a blue color which persists for 30 seconds. Calculate the I_2 normality as:

$$\text{Normality } I_2 = \frac{\text{ml } As_2O_3 \times \text{Normality } As_2O_3}{\text{ml } I_2} \tag{4}$$

3.7.2 Method B. Pipet accurately 50 ml standard potassium iodate solution into a 100-ml volumetric flask. Add 2 g KI and 10 ml 1 N sulfuric acid and dilute to volume with purified water and mix thoroughly. Prepare fresh as required. Calculate the I_2 normality as:

$$\text{Normality } I_2 = \text{Normality } KIO_3 \times \frac{50}{100} \tag{5}$$

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3.8 Diluted standard iodine solution. Immediately before use, pipet 10 ml standard iodine solution into a 100-ml volumetric flask and dilute to volume with absorbing reagent. Then pipet 5 ml of this solution into a 100-ml volumetric flask and dilute to volume with absorbing reagent.

4. Procedure.

4.1 Assemble an ozone calibration system such as shown in Figure 1.

4.2 Assemble the KI sampling train as shown in Figure 2. Use ground-glass connections upstream from the impingers.

4.3 Ensure that all flowmeters are calibrated under the conditions of use against a reliable standard such as a soap-bubble meter or wet-test meter traceable to NBS. All volumetric flowrates should be corrected to 25° C and 760 mm Hg. A detailed discussion on proper calibration of flowmeters is given in Reference 4.

4.4 KI calibration curve.

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EPA-287 (Cin.)
(4-75)

4.4.1 Into a series of 25-ml volumetric flasks, pipet 1, 2, 3, 4, and 5 ml of diluted standard iodine solution (see Step 3.8). Dilute each to volume with absorbing reagent. Mix thoroughly, transfer to a clean 1-cm cell, and read the absorbance of each solution at 352 nm against purified water as the reference. The containers should remain stoppered until the absorbance is read to prevent I_2 losses by volatilization. Read the absorbance of unexposed absorbing reagent against purified water as the reference.

4.4.2 Calculate the concentration of the solutions as total μg O_3 as follows:

$$\text{Total } \mu g\ O_3 = (N)\ (48)\ (V_1) \qquad (6)$$

where: N = normality I_2 (see Step 3.7.1 or 3.7.2), meg/ml
V_1 = volume of diluted standard I_2 added, ml (1, 2, 3, 4, 5)

4.4.3 Plot net absorbance (sample-reagent blank) versus total μg O_3 and draw the KI calibration curve.

4.5 Calibration of the ozone generator.

4.5.1 Adjust the air flow through the O_3 generator to the desired flowrate and record as F_0. At all times the air flow through the generator must be greater than the total flow required by the sampling systems.

4.5.2 With the ozone generator off, flush the system for several minutes to remove residual ozone. Pipet 10 ml absorbing reagent into each impinger. Draw air from the output manifold of the O_3 calibration system through the sampling train at 0.4 - 0.6 l/min for 10 minutes. Immediately transfer the exposed solution to a clean 1-cm cell. Determine the absorbance at 352 nm within three minutes against purified water as the reference. Determine the net absorbance (sample-

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

reagent blank). If the system blank gives a net absorbance, continue flushing the ozone generation system until no net absorbance is obtained.

4.5.3 Adjust the O_3 generator to generate an O_3 concentration in the range of interest (0.05 to 0.5 ppm) and allow the system to equilibrate for about 10 minutes. The uncalibrated chemiluminescence O_3 analyzer can conveniently be used to indicate the stability of the O_3 generator output. When the O_3 generator output has stabilized, pipet 10 ml of absorbing reagent into each impinger and sample for 10 to 15 minutes. Immediately transfer the solutions from the two absorbers to clean 1-cm cells. Determine the absorbance of each at 352 nm within three minutes against purified water as the reference. Add the net absorbances (sample-reagent blank) of the two solutions to obtain total absorbance. Read total μg O_3 from the KI calibration curve (see Step 4.4). Calculate the total volume of air sampled corrected to reference conditions of 25° C and 760 mm Hg as follows:

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$$V_R = V \times \frac{P}{760} \times \frac{298}{T + 273} \qquad (7)$$

where: V_R = volume of air at reference conditions, liter
V = volume of air at sampling conditions, liter
P = barometric pressure at sampling conditions, mm Hg
T = temperature at sampling conditions, °C

Calculate the O_3 concentration in ppm as follows:

$$\text{ppm } O_3 = \frac{\mu g\ O_3}{V_R} \times 0.510 \qquad (8)$$

Repeat the above procedure at least one time. Average the two (or more) determinations and record along with the O_3 generator setting.

4.5.4 Adjust the O_3 generator to obtain other O_3 concentrations over the desired range. Determine each O_3 concentration using the procedure

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EPA-287 (Cin.)
(4-76)

given above and calculate each concentration using Equation 8. Five or more O_3 concentrations are recommended. Plot the O_3 concentration versus the O_3 generator setting and draw the O_3 generator calibration curve.

4.6 Calibration of the ozone analyzer.

4.6.1 Allow sufficient time for the O_3 analyzer to warm-up and stabilize.

4.6.2 Allow the O_3 analyzer to sample zero air until a stable response is obtained and adjust the O_3 analyzer's zero control. Offsetting the analyzer's zero adjustment to + 5 percent of scale is recommended to facilitiate observing negative zero drift. Record the stable zero air response as "Z".

4.6.3 Using the O_3 generator as calibrated above, and the same F_0, generate an O_3 concentration near 80 percent of the desired URL of the analyzer.

4.6.4 Allow the O_3 analyzer to sample this O_3 concentration until a stable response is obtained. Adjust the analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{OUT}}{URL} \times 100\right) + Z \qquad (9)$$

where: URL = upper range limit of the O_3 analyzer, ppm
Z = recorder response with zero air, % scale

Record the O_3 concentration and the analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating Steps 4.6.2 and 4.6.4.

BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
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PAGE NUMBER

EPA-287 (Cin.)
(4-76)

4.6.5 Generate several other O_3 concentrations (at least five others are recommended) over the scale range of the analyzer by adjusting the O_3 generator settings (preferably the same settings as used in Step 4.5.4). For each O_3 concentration, allow for a stable analyzer response, then record the response and the corresponding O_3 concentration.

4.6.6 Plot the O_3 analyzer responses versus the corresponding O_3 concentrations and draw the O_3 analyzer's calibration curve or calculate the appropriate response factor.

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EPA-287 (Cin.)
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2. Transfer Standards for Ozone Concentrations. EPA Publication (to be prepared).

3. Lodge, J.P. Jr., J.B. Pate, B.E. Ammons, and G.A. Swanson. The Use of Hypodermic Needles as Critical Orifices in Air Sampling. J. Air Pollut. Control Assoc., 16, 197 (1966).

4. Technical Assistance Document for the Chemiluminescence Measurement of Ozone. EPA Publication (to be prepared).

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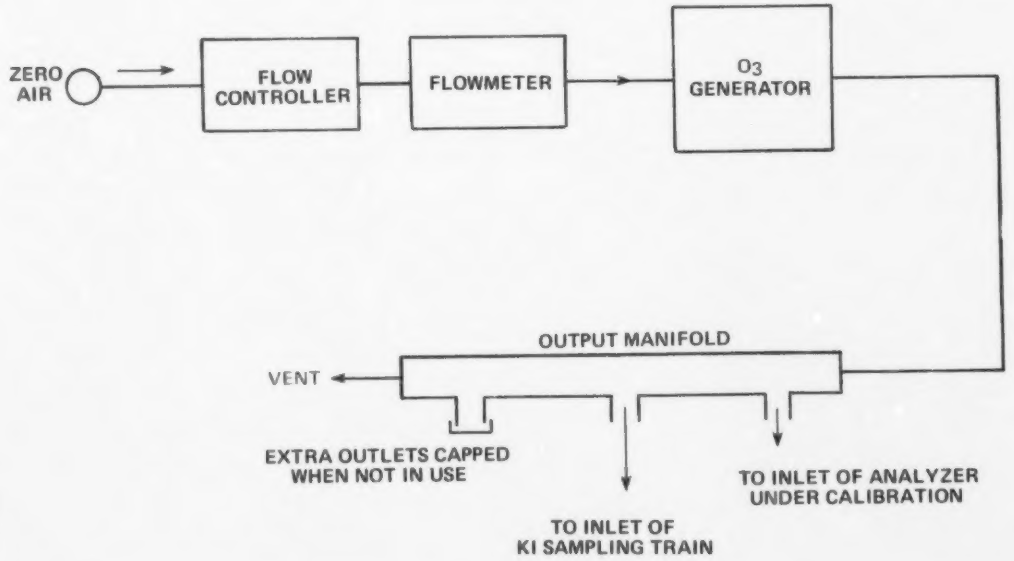
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FLOW CONTROLLER
FLOWMETER
O_3 GENERATOR
OUTPUT MANIFOLD
VENT
EXTRA OUTLETS CAPPED WHEN NOT IN USE
TO INLET OF KI SAMPLING TRAIN
TO INLET OF ANALYZER UNDER CALIBRATION

Figure 1. Schematic diagram of a typical O_3 calibration system.

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EPA-287 (Cin.)
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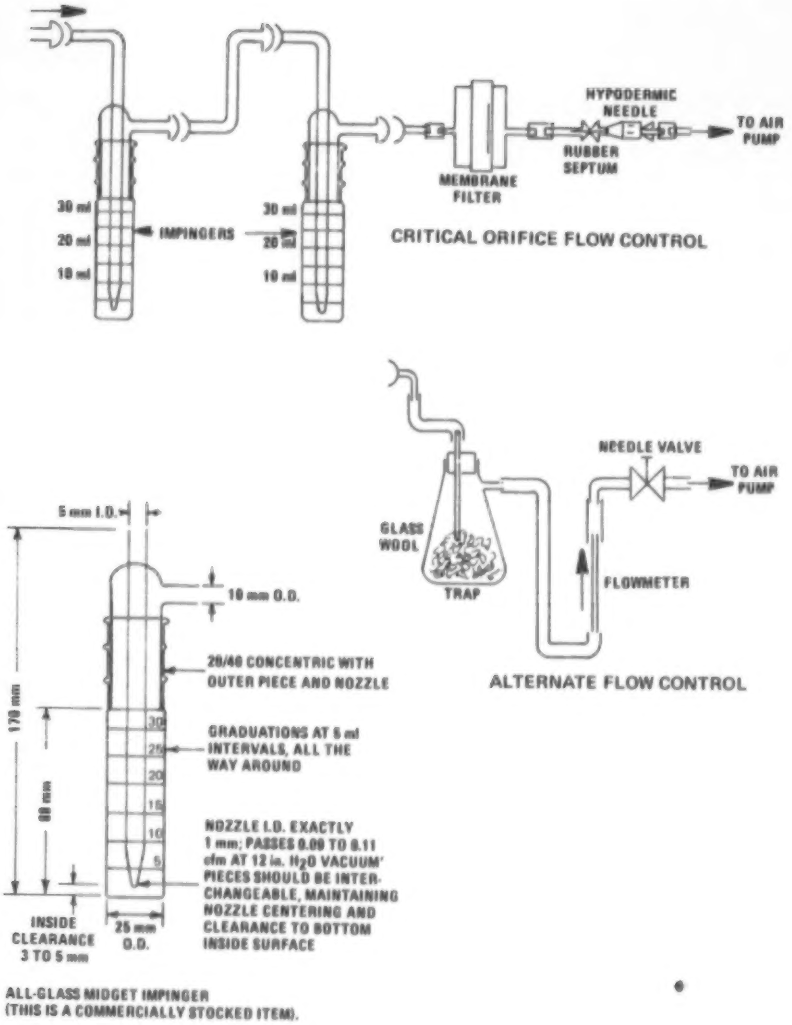
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IMPINGERS
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MEMBRANE FILTER
HYPODERMIC NEEDLE
RUBBER SEPTUM
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CRITICAL ORIFICE FLOW CONTROL
NEEDLE VALVE
TO AIR PUMP
GLASS WOOL
TRAP
FLOWMETER
ALTERNATE FLOW CONTROL
5 mm I.D.
10 mm O.D.
170 mm
80 mm
20/40 CONCENTRIC WITH OUTER PIECE AND NOZZLE
30
25
20
15
10
5
GRADUATIONS AT 5 ml INTERVALS, ALL THE WAY AROUND
NOZZLE I.D. EXACTLY 1 mm; PASSES 0.09 TO 0.11 cfm AT 12 in. H2O VACUUM' PIECES SHOULD BE INTERCHANGEABLE, MAINTAINING NOZZLE CENTERING AND CLEARANCE TO BOTTOM INSIDE SURFACE
INSIDE CLEARANCE 3 TO 5 mm
25 mm O.D.
ALL-GLASS MIDGET IMPINGER
(THIS IS A COMMERCIALLY STOCKED ITEM).

Figure 2. Diagram of KI sampling train.

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

APPENDIX E

TENTATIVE CALIBRATION PROCEDURE USING BORIC ACID-POTASSIUM IODIDE (BAKI)

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PAGE NUMBER
EPA-287 (Cin.)
(4-78)

APPENDIX E

TENTATIVE CALIBRATION PROCEDURE USING BORIC ACID-POTASSIUM IODIDE (BAKI) (REVISED)

Major Equipment Required: Stable ozone generator, spectrophotometer

1. Principle.

1.1 The calibration procedure is based upon the reaction between ozone (O_3) and potassium iodide (KI) to release iodine (I_2) according to the stoichiometric equation:(1)

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$$O_3 + 2I^- + 2H^+ \rightarrow I_2 + H_2O + O_2 \qquad (1)$$

The stoichiometry is such that the amounts of O_3 absorbed and iodine (I_2) released are equivalent. Ozone is absorbed in a 0.1 M boric acid solution containing 1 percent KI and the I_2 released is measured spectrophotometrically as the triiodide ion (I_3^-) at 352 nm. The output of a stable O_3 generator is determined in this manner and the generator is subsequently used to calibrate the chemiluminescence O_3 analyzer. The O_3 generator is normally used immediately after calibration and without physical movement, and is recalibrated prior to each use. If the O_3 generator is to be used at other times without recalibration, or at other locations as a transfer standard, it must meet the requirements and specifications set forth in Reference 2, "Transfer Standards for Ozone Concentrations."

2. Apparatus. Figure 1, a schematic of a typical O_3 calibration system, shows the suggested configuration of the components listed below. All connections between components downstream from the O_3 generator should be

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(4-76)

of glass, Teflon®, or other non-reactive material. Additional information regarding the assembly of a calibration system is given in Reference 3.

2.1 Air flow controller. Device capable of maintaining constant air flowrate through the O_3 generator within ± 2 percent.

2.2 Air flowmeter. Calibrated flowmeter capable of measuring and monitoring air flowrate through the O_3 generator within ± 2 percent.

2.3 Ozone generator. Device capable of generating stable levels of O_3 over the required concentration range.

2.4 Output manifold. The output manifold should be constructed of glass, Teflon®, or other non-reactive material and should be of sufficient diameter to ensure an insignificant pressure drop at the analyzer connection. The system must have a vent designed to ensure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

2.5 Impingers. All glass impingers with the specifications indicated in Figure 2 are recommended. The impingers may be purchased from most major glassware suppliers. Two absorbers in series are needed to ensure complete collection of the sample.

2.6 Air pump and flow controller. Any pump and flow control device capable of maintaining a constant flow of 0.4-0.6 l/min through the impingers may be used. A critical orifice as described by Lodge(4) is recommended. The orifice should be protected against moisture and particulate matter with a Drierite® or silica gel trap. The air pump should be capable of maintaining a pressure differential of 0.6-0.7 atmospheres across the critical orifice. Alternatively, a needle valve could be used with the pump to control the flow through the impingers. A flowmeter is then recommended to monitor the flow and the needle valve-flowmeter combination should be protected against moisture and particulate matter with a Drierite® or silica gel trap.

2.7 Thermometer. Accurate to ± 1° C.

2.8 Barometer. Accurate to ± 2 mm Hg.

2.9 Volumetric flasks (Class A). 25, 100, 1000-ml.

2.10 Pipets (Class A). 5, 10, 15, 20, 25, and 50-ml volumetric.

2.11 Spectrophotometer. Capable of measuring absorbance at 352 nm with an absolute accuracy of ± 1 percent and linear response over the range of 0-0.9 absorbance units. Matched 1-cm or 2-cm cells should be used.

3. Reagents.

3.1 Zero air. The air must be free of contaminants which will cause a detectable response on the O_3 analyzer or which might react with 1 percent BAKI. Air meeting this requirement is obtained by: (1) passing it through silica gel for drying; (2) treating with ozone to convert any NO to NO_2; (3) passing it through activated charcoal (6-14 mesh) and molecular sieve (6-16 mesh, type 4A) to remove any NO_2, hydrocarbons and traces of water vapor; and (4) passing it through a 2-micron filter to remove any particulate matter. When calibrating an O_3 generator as a transfer standard, zero air should be obtained from an ambient air source, as other sources of air may vary in oxygen content, which would affect the accuracy of the transfer standard.

3.2 Distilled water. Used for all reagents.

3.3 Absorbing reagent. Dissolve 6.2 g of certified ACS grade boric acid (H_3BO_3) in approximately 750 ml of distilled water in a nonactinometric 1000-ml volumetric flask. The flask may be heated gently

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3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

to speed dissolution of the boric acid but the solution must then be cooled to room temperature or below before proceeding with the reagent preparation. While the boric acid solution is cooling, prepare the hydrogen peroxide (H_2O_2) solution according to the directions in Step 3.4. When the boric acid solution has cooled, add 10 g of certified ACS grade potassium iodide (KI) to the boric acid solution and dissolve. Add 1 ml of 0.0018 percent H_2O_2 solution and mix thoroughly. Within 5 minutes after adding the peroxide: (1) dilute to volume with distilled water and mix, and (2) determine the absorbance of this BAKI solution at 352 nm against distilled water as the reference. The pH of the BAKI solution should be 5.5 ± 0.2.

Set the absorbing solution aside for 2 hours. Redetermine the absorbance at 352 nm against distilled water as the reference. If the resultant absorbance from this second determination is at least 0.010 absorbance units/cm greater than the first determination, the absorbing reagent is ready for use. If no increase or an increase of less than 0.010 absorbance units/cm is observed, the KI reagent probably contains an excessive amount of a reducing contaminant and must be discarded. In this event, prepare fresh absorbing reagent using a different numbered lot of certified ACS grade KI. If unacceptable absorbing reagent results from different lots of KI, test the possibility of contamination in the boric acid by using a different numbered lot of certified ACS grade H_3BO_3.

3.4 Hydrogen peroxide solution (0.0018 percent). Add 3 ml of 30 percent or 30 ml of 3 percent certified ACS grade hydrogen peroxide (H_2O_2) to approximately 200 ml of distilled water in a 1000-ml volumetric flask and dilute to volume with distilled water and mix thoroughly. To prepare the 0.0018 percent solution, add 2 ml of the above solution to 50 ml of distilled water in a 100-ml volumetric flask and dilute to volume with distilled water and mix thoroughly. This 0.0018 percent H_2O_2 solution must be prepared fresh each time a fresh batch of absorbing reagent is prepared. Therefore, the remaining contents of both volumetric flasks should be discarded after treatment of the BAKI absorbing reagent (see Step 3.3).

EPA-287 (Cin.)
(4-76)

3.5 Standard potassium iodate solution (0.1 N). A commercial certified standard solution of potassium iodate (KIO_3) must be used.

3.6 Sulfuric acid (1 N). Dilute 28 ml of concentrated (95-98 percent) reagent grade sulfuric acid (H_2SO_4) to volume in a 1000-ml volumetric flask.

4. Procedure.

4.1 Assemble an ozone calibration system such as shown in Figure 1.

4.2 Assemble the KI sampling train such as shown in Figure 2. All connections between the various components should be leak tight and may be made using grease-free ball joint fittings, heat-shrinkable Teflon® tubing, or Teflon® tube fittings. The connection to the O_3 output manifold should be made using 1/4 in. Teflon® tubing not to exceed 4 ft. in length.

4.3 All flowmeters must be calibrated under the conditions of use against a reliable standard such as a soap-bubble meter or wet-test meter traceable to NBS. All volumetric flowrates should be corrected to 25° C and 760 mm Hg. A detailed discussion on proper calibration of flowmeters is given in Reference 3.

4.4 KI calibration curve.

4.4.1 Iodine standards. Prepare fresh as required.

4.4.1.1 Accurately pipet 10 ml of 0.1 N standard potassium iodate solution into a 100-ml volumetric flask. Add 1 g of certified ACS grade potassium iodide (KI) and 5 ml of 1 N sulfuric acid and dilute to volume with distilled water and mix thoroughly.

4.4.1.2 Immediately before use, pipet 10 ml of the iodine solution prepared in Step 4.4.1.2 above into a 100-ml volumetric flask and dilute

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

to volume with absorbing reagent. Then pipet 5 ml of this solution into a 100-ml volumetric flask and dilute to volume with absorbing reagent.

4.4.1.3 Pipet 5, 10, 15, 20, and 25 ml of the iodine solution prepared in Step 4.4.1.2 above into a series of 25-ml volumetric flasks. Dilute each to volume with absorbing reagent and mix thoroughly. To prevent I_2 losses by volatilization, the flasks should remain stoppered until absorbance measurements are made. All absorbance measurements should be taken within 20 minutes after preparation of the iodine standards.

4.4.2 Determine the absorbance of each iodine standard at 352 nm. Also measure the absorbance of a sample of unexposed absorbing reagent. Determine the net absorbance of each iodine standard as:

$$\text{net absorbance} = \left(\begin{array}{c}\text{sample}\\ \text{absorbance}\end{array} - \begin{array}{c}\text{unexposed}\\ \text{reagent}\\ \text{absorbance}\end{array} \right) \qquad (2)$$

4.4.3 For each iodine standard, calculate the net absorbance/cm as:

$$\text{net absorbance/cm} = \frac{\text{net absorbance}}{b} \qquad (3)$$

where: b = spectrophotometer cell pathlength, cm

4.4.4 For each iodine standard, calculate the iodine concentration in mole/l as:

$$[I_2]_i = \text{normality } KIO_3 \times \frac{1 \text{ eq } I_2}{1 \text{ eq } KIO_3} \times \frac{1 \text{ mole } I_2}{2 \text{ eq } I_2} \times \frac{10}{100} \times \frac{10}{100} \times \frac{5}{100} \times \frac{V_i}{25} \qquad (4)$$

$$[I_2]_i = \text{normality } KIO_3 \times V_i \times 10^{-5} \qquad (5)$$

where: $[I_2]_i$ = concentration of each I_2 standard, mole/l

normality KIO_3 = normality of KIO_3 (from Step 3.5), eq/l

V_i = volume of I_2 solution (from 4.4.1.3), 5, 10, 15, 20, and 25 ml.

BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

4.4.5 Plot net absorbance/cm (y-axis) versus the mole I_2/l (x-axis) for each iodine standard and draw the KI calibration curve. Calculate the slope of the curve in l $mole^{-1}cm^{-1}$ and record as S_c. The value of the slope should be 25,600 ± 600.

4.5 Calibration of the ozone generator.

4.5.1 Adjust the air flow through the O_3 generator to the desired flowrate and record as F_0. At all times the air flow through the generator must be greater than the total flow required by the sampling systems.

4.5.2 With the ozone generator off, flush the system for at least 15 minutes to remove residual ozone. Pipet 10 ml of absorbing reagent into each impinger. Draw air from the output manifold of the O_3 calibration system through the sampling train at 0.4-0.6 l/min for 10 minutes. Immediately transfer the exposed solutions to clean spectrophotometer cells. Determine the net absorbance (sample absorbance-unexposed reagent absorbance) of each solution at 352 nm within three minutes. Add the net absorbances of the two solutions to obtain the total net absorbance. Calculate the system blank as equivalent O_3 concentration according to Step 4.5.4. If the system blank is greater than 0.005 ppm O_3, continue flushing the ozone generation system for an additional 30 minutes and redetermine the system blank. If the system blank is still greater than 0.005 ppm O_3, the zero air probably contains traces of an oxidizing contaminant and the activated charcoal and molecular sieve (see Step 3.1) should be replaced.

4.5.3 Adjust the O_3 generator to generate an O_3 concentration in the range of interest (0.05 to 0.5 ppm) and allow the system to equilibrate for about 15 minutes. The uncalibrated chemiluminescence O_3 analyzer can conveniently be used to indicate the stability of the O_3 generator output. When the O_3 generator output has stabilized, pipet 10 ml of absorbing reagent into each impinger. Draw O_3 from the output manifold of the O_3 calibration system through the sampling train at 0.4-0.6 l/min. Select a sample time of 10 minutes or greater such that a total net absorbance

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BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

greater than 0.100 absorbance units is obtained. At an O_3 concentration of 0.1 ppm and a sampling rate of 0.5 l/min, a total net absorbance $\geq$ 0.1 absorbance units should be obtained if a sampling time of 20 minutes and 1-cm spectrophotometer cells are used. Immediately after collection, transfer the exposed solutions to clean spectrophotometer cells. Determine the net absorbance (sample absorbance-unexposed reagent absorbance) of each solution at 352 nm within three minutes. Add the net absorbances of the two solutions to obtain the total net absorbance.

4.5.4 Calculation of ozone concentration.

4.5.4.1 Calculate the total volume of air sampled corrected to reference conditions of 25° C and 760 mm Hg as:

$$V_R = V_S \times \frac{P_S}{760} \times \frac{298}{T_S + 273} \qquad (6)$$

where: V_R = volume of air at reference conditions, l
V_S = volume of air at sampling conditions, l
P_S = barometric pressure at sampling conditions, mm Hg
T_S = temperature at sampling conditions, °C

4.5.4.2 Calculate the mole of I_2 released as:

$$\text{mole } I_2 = \frac{\text{total net absorbance} \times 0.01}{S_C \times b} \qquad (7)$$

where: total net absorbance = sum of net absorbances for the two solutions
0.01 = volume of absorbing reagent in each impinger, l
S_C = slope of KI calibration curve, l $\text{mole}^{-1}\text{cm}^{-1}$
b = spectrophotometer cell pathlength, cm

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER

4.5.4.3 Calculate the μl of O_3 absorbed as:

$$\mu l\ O_3 = \text{mole } I_2 \times \frac{1 \text{ mole } O_3}{1 \text{ mole } I_2} \times \frac{24.47 \text{ l } O_3}{\text{mole } O_3} \times \frac{10^6\ \mu l\ O_3}{l\ O_3} \tag{8}$$

$$\mu l\ O_3 = \text{mole } I_2 \times 24.47 \times 10 \tag{9}$$

4.5.4.4 Calculate the O_3 concentration in ppm as:

$$\text{ppm } O_3 = \frac{\mu l\ O_3}{V_R} \tag{10}$$

4.5.5 Repeat Steps 4.5.3 and 4.5.4 at least one more time. Average the two (or more) determinations and record along with the O_3 generator setting.

4.5.6 Adjust the O_3 generator to obtain other O_3 concentrations over the desired range. Determine each O_3 concentration using the procedure given above and calculate each concentration using Equation 10. Five or more O_3 concentrations are recommended. Plot the O_3 concentration versus the O_3 generator setting and draw the O_3 generator calibration curve.

4.6 Calibration of the ozone analyzer.

4.6.1 Allow sufficient time for the O_3 analyzer to warm-up and stabilize.

4.6.2 Allow the O_3 analyzer to sample zero air until a stable response is obtained and adjust the O_3 analyzer's zero control. Offsetting the analyzer's zero adjustment to + 5 percent of scale is recommended to facilitate observing negative zero drift. Record the stable zero air response as "Z".

4.6.3 Using the O_3 generator as calibrated above, and the same F_0, generate an O_3 concentration near 80 percent of the desired upper range

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

limit (URL) of the analyzer.

4.6.4 Allow the O_3 analyzer to sample this O_3 concentration until a stable response is obtained. Adjust the analyzer's span control to obtain a convenient recorder response as indicated below:

$$\text{recorder response (\% scale)} = \left(\frac{[O_3]_{OUT}}{URL} \times 100\right) + Z \qquad (11)$$

where: $[O_3]_{OUT}$ = O_3 concentration at the output manifold, ppm
URL = upper range limit of the O_3 analyzer, ppm
Z = recorder response with zero air, % scale

Record the O_3 concentration and the analyzer response. If substantial adjustment of the span control is necessary, recheck the zero and span adjustments by repeating Steps 4.6.2 through 4.6.4.

9-1/8"

4.6.5 Generate several other O_3 concentrations (at least five others are recommended) over the scale range of the analyzer by adjusting the O_3 generator settings (preferably the same settings as used in Step 4.5). For each O_3 concentration, allow for a stable analyzer response, then record the response and the corresponding O_3 concentration.

4.6.6 Plot the O_3 analyzer responses versus the corresponding O_3 concentrations and draw the O_3 analyzer's calibration curve or calculate the appropriate response factor.

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BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

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2. Transfer Standards for Ozone Concentrations. EPA Publication (to be prepared).

3. Technical Assistance Document for the Chemiluminescence Measurement of Ozone. EPA Publication (to be prepared).

4. Lodge, J. P., Jr., J. B. Pate, B. E. Ammons, and G. A. Swanson. The Use of Hypodermic Needles as Critical Orifices in Air Sampling. J. Air Pollut. Control Assoc., 16, 197 (1966).

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BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

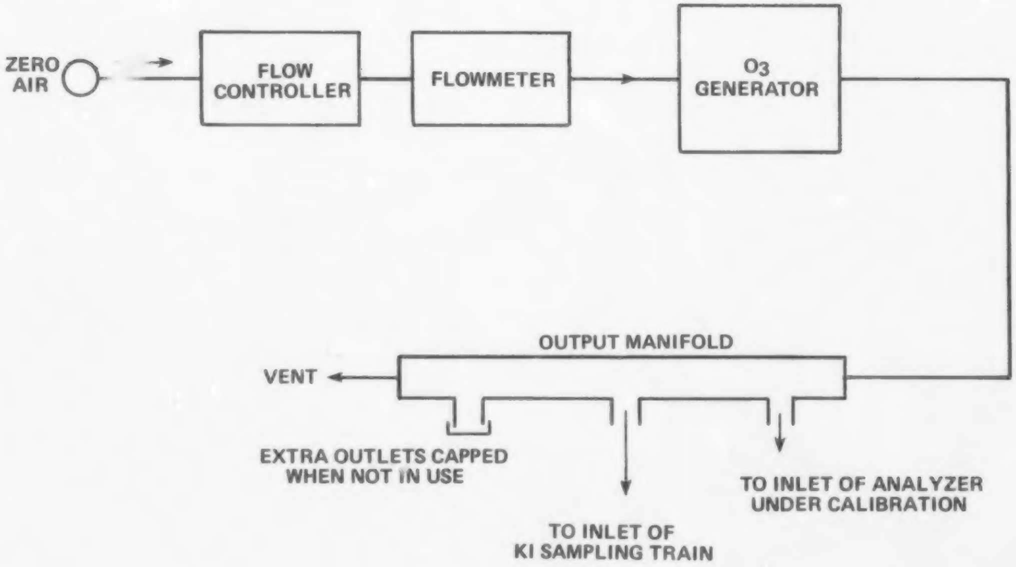
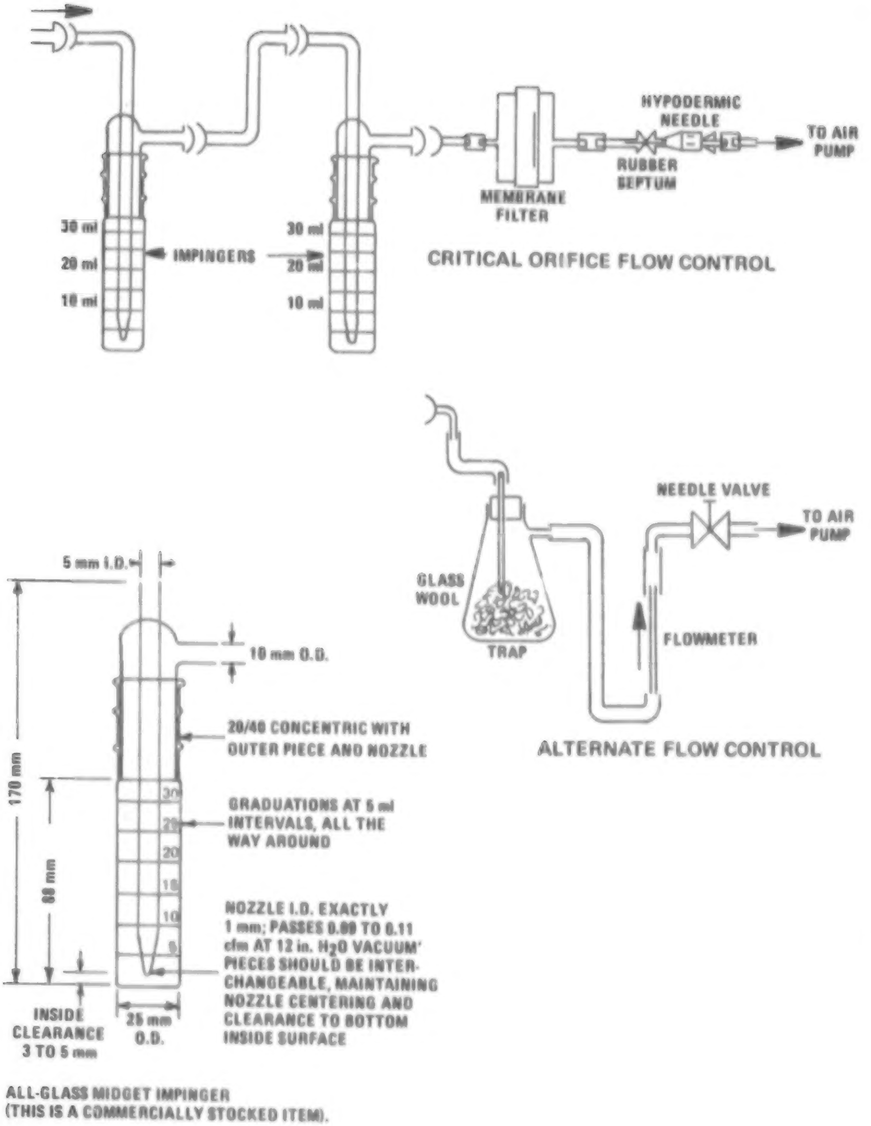

ZERO AIR
FLOW CONTROLLER
FLOWMETER
O_3 GENERATOR
OUTPUT MANIFOLD
VENT
EXTRA OUTLETS CAPPED WHEN NOT IN USE
TO INLET OF KI SAMPLING TRAIN
TO INLET OF ANALYZER UNDER CALIBRATION

Figure 1. Schematic diagram of a typical O_3 calibration system.


IMPINGERS
30 ml
20 ml
10 ml
30 ml
20 ml
10 ml
MEMBRANE FILTER
HYPODERMIC NEEDLE
RUBBER SEPTUM
TO AIR PUMP
CRITICAL ORIFICE FLOW CONTROL
GLASS WOOL
TRAP
NEEDLE VALVE
TO AIR PUMP
FLOWMETER
ALTERNATE FLOW CONTROL
5 mm I.D.
10 mm O.D.
170 mm
80 mm
20/40 CONCENTRIC WITH OUTER PIECE AND NOZZLE
30
25
20
15
10
5
GRADUATIONS AT 5 ml INTERVALS, ALL THE WAY AROUND
NOZZLE I.D. EXACTLY 1 mm; PASSES 0.09 TO 0.11 cfm AT 12 in. H2O VACUUM' PIECES SHOULD BE INTERCHANGEABLE, MAINTAINING NOZZLE CENTERING AND CLEARANCE TO BOTTOM INSIDE SURFACE
INSIDE CLEARANCE 3 TO 5 mm
25 mm O.D.
ALL-GLASS MIDGET IMPINGER (THIS IS A COMMERCIALLY STOCKED ITEM).

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BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

Figure 2. Diagram of KI sampling train.

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

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3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

APPENDIX F

VOLUNTEERS AND VOLUNTEER OZONE CALIBRATION SYSTEMS

APPENDIX F

VOLUNTEERS AND VOLUNTEER OZONE CALIBRATION SYSTEMS

VOLUNTEERS FOR ULTRAVIOLET PHOTOMETRY

The volunteers who participated in the ultraviolet photometry (UV) variability study and their affiliation are listed below.

1. Michael E. Beard

   Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

2. Oscar L. Dowler

   Health Effects Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

3. Bobbie A. Grimes

   Research Triangle Institute, Research Triangle Park, North Carolina.

4. Richard J. Paur

   Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

5. Kenneth A. Rehme

   Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

VOLUNTEERS FOR GAS PHASE TITRATION WITH EXCESS NITRIC OXIDE

The volunteers who participated in the gas phase titration with excess nitric oxide (GPT-NO) variability study and their affiliation are listed below. A brief description of their GPT calibration systems follows.

1. Glenn R. Ballard

   Health Effects Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

   Bendix Model 8861 Portable Field Calibration System:

   Modified zero air system by adding a larger charcoal scrubber, a Permapure dryer, and indicating dessicant column. Pressure gauges and capillaries removed and replaced with Tylan miniature flow controllers with digital readout. Installed quick disconnect fittings for zero air, ozone generator air, and NO calibration gas.

2. Michael E. Beard

   Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

   Operator Assembled GPT Calibration System:

   National Bureau of Standards (NBS) prototype O_3 generator with mechanical sleeve used with glass and Teflon® GPT system. Kjeldahl mixing bulbs used for reaction and dilution chambers. Flows controlled by needle valves and air supplied by Bendix Model 8834 Zero Air System. Output air passed through ozonator and scrubbers containing charcoal, molecular sieve, and silica gel.

3. Jack A. Bowen

   Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

EPA-287 (Cin.)
(4-78)

Bendix Model 8851 Dynamic Calibration System:

Modified to allow for O_3 generator air flow control by Input A pressure regulator. Capillary and regulator for NO calibration gas replaced. Zero air system uses ozonator with silica gel and charcoal-soda lime scrubbing columns.

4. Oscar L. Dowler

Health Effects Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Operator Assembled GPT Calibration System:

South States O_3 generator with mechanical sleeve used with unibody glass GPT reaction and mixing chambers. F_O, F_D, F_{NO} controlled by Tylan mass flow controllers with digital readout. Zero air system with ozonator and charcoal and molecular sieve scrubbers.

5. Bobbie A. Grimes

Research Triangle Institute, Research Triangle Park, North Carolina.

Operator Assembled GPT Calibration System:

South States O_3 generator with glass and Teflon® GPT system. Flow controlled by needle valves and monitored with rotameters. Zero air system consisted of gas pump with regulator and silica gel, pura-fil, Drierite®, molecular sieve, and charcoal scrubbers.

6. Lawrence T. Hackworth

Research Triangle Institute, Research Triangle Park, North Carolina.

Operator Assembled GPT Calibration System:

Same type as used by Bobbie A. Grimes above.

7. Paul J. Haskins

Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Bendix Model 8861 Portable Field Calibration System:

Modified according to procedures in Attachment 1.

8. Kenneth A. Rehme

Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Bendix Model 8851 Dynamic Calibration System:

Modified in same way as GPT system used by Jack A. Bowen above. Zero air supplied by test laboratory zero air supply system.

9. Vinson L. Thompson

Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Thermo Electron Series 101 Dynamic NO/NO$_2$/O$_3$ Calibrator:

Zero air input regulator replaced with Fairchild Model 10 regulator. Dilution air capillary shortened to obtain higher flow rate.

10. John A. Wall

Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Bendix Model 8861 Portable Field Calibration System:

Modified according to procedures in Attachment 1.

EPA-287 (Cin.)
(4-76)

Attachment 1, Modifications to the Bendix Model 8861 Calibration System

1. Replace the 0-15 psi NO pressure gauge with a 0-27 psi. Dismantle the ozone generator-flow capillary compartment and replace capillary No. 1 (NO flow) with one that will give a flow rate of about 20 cc/min at 25 psig. A greater concentration of NO can thus be obtained through the calibration system at the specified dilution flow rates.

2. While the compartment is dismantled, plug the orifice that controls the flow through the ozone generator. Connect a capillary (500 cc/min at 25 psig) to the inlet of the ozone generator. Connect 1/8 in. Teflon® tubing to the other end of the capillary. Close the compartment, leaving the capillary inside but bringing the end of the Teflon® tubing outside the compartment. Connect an additional pressure regulator and gauge (0-25 psi, similar to original equipment preferred) to the zero air supply up-stream from the existing regulator and gauge that controls the dilution air flow. Connect the Teflon® tubing to the outlet of the pressure regulator just installed. This modification allows the flow through the ozone generator to be controlled separately by the new regulator and gauge (Input A). It is needed primarily for the reverse gas phase titration calibration of ozone instruments. It is not essential in the calibration of $NO/NO_2/NO_x$ instruments.

3. Remove the condensing coil from the system. Cut the electrical wires to the fan and remove it from the system. Insulate the ends of the wires just cut. Install a silica gel scrubber (.5 l or larger) in line between the water drop-out and the clean-up lamp. This will give a dryer calibration air than the condenser-fan assembly.

4. Replace the charcoal-soda lime filter down-stream from the surge tank with a larger one (.5 l or larger). The scrubber material will have to be changed less often.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

VOLUNTEERS FOR GAS PHASE TITRATION WITH EXCESS OZONE

The volunteers who participated in the gas phase titration with excess ozone (GPT-O_3) variability study and their affiliation are listed below. A brief description of their GPT calibration systems follows.

1. Glenn R. Ballard

   Health Effects Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

   Bendix Model 8861 Portable Field Calibration System:
   Modified to include Tylan mass flow controllers.

2. Jack A. Bowen

   Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

   Bendix Model 8851 Dynamic Calibration System:
   Modified to provide flow control as required for GPT-O_3 procedure.

3. Wayne E. Brown

   Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

   Bendix Model 8861 Portable Field Calibration System:
   Modified to include Tylan mass flow controllers.

4. Connie F. Turlington

   Research Triangle Institute, Research Triangle Park, North Carolina.

   Operator Assembled GPT Calibration System:
   O_3 generator with movable sleeve, Kjeldahl mixing bulbs for reaction and dilution chambers, and needle valves for flow control.

5. Bobbie A. Grimes

Research Triangle Institute, Research Triangle Park, North Carolina.

Similar apparatus to Number 4.

6. Lawrence T. Hackworth

Research Triangle Institute, Research Triangle Park, North Carolina.

Similar apparatus to Number 4.

7. Thomas A. Lumpkin

Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Bendix Model 8861 Portable Field Calibration System:
Modified to include Tylan mass flow controllers.

8. Willie T. McLeod

Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Bendix Model 8861 Portable Field Calibration System:
Modified to include Tylan mass flow controllers.

9. Kenneth A. Rehme

Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Bendix Model 8851 Dynamic Calibration System:
Modified to provide flow control as required for GPT-O_3 procedure.

10. Vinson L. Thompson

    Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Thermo Electron Series 101 Dynamic $NO/NO_2/O_3$ Calibrator:
Modified to permit required flow rates.

VOLUNTEERS FOR BORIC ACID-POTASSIUM IODIDE

The volunteers who participated in the BAKI variability study and their affiliation are listed below.

Research Triangle Park Volunteers

1. Jack A. Bowen

   U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina.

2. Oscar L. Dowler

   U.S. Environmental Protection Agency, Health Effects Research Laboratory, Research Triangle Park, North Carolina.

3. Connie F. Turlington

   U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina.

4. Bobbie A. Grimes

   Research Triangle Institute, Research Triangle Park, North Carolina.

5. C. Frederick Smith

   U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina.

6. Vinson L. Thompson

   U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina.

EPA-287 (Cin.)
(4-76)

7. Ann Turner

   Research Triangle Institute, Research Triangle Park, North Carolina.

Field Volunteers

1. Dennis Anderson and Mark Cher

   Rockwell International, Atomics International Division, Air Monitoring Center, Newbury Park, California.

2. Barbara Dell'Aqua and Edward Legere

   State of New York, Department of Health, Division of Laboratories and Research, Environmental Health Center, Albany, New York.

   Frank Buckman and Robert Kerr

   State of New York, Department of Environmental Conservation, Division of Air Resources, Albany, New York.

3. Donald Tingle and Diana Andrews

   Kentucky Department of Natural Resources and Environmental Protection, Division of Air Pollution, Frankfort, Kentucky.

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3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

APPENDIX G

TEST LABORATORY PREPARATION FOR VARIABILITY STUDIES

9-1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

APPENDIX G

TEST LABORATORY PREPARATION FOR VARIABILITY STUDIES

REFERENCE SYSTEM

Ultraviolet Photometers

A Dasibi Model 1003-AH Ozone (O_3) Monitor (S/N 1137), modified to operate as an absolute O_3 photometer, was compared to the Quality Assurance Division (QAD), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, photometer prior to and at the completion of the studies. The Dasibi photometer set-up data and the results of the comparison with the QAD photometer are given in Tables G-1 and G-2.

TABLE G-1. DASIBI PHOTOMETER SET-UP

Set-Up Identification/Function	Number/Data
Model number	S/N 1137
Span number	50.730
Sample frequency	46.4
Control frequency	24.1
Sample flow	2.08 l/min

TABLE G-2. COMPARISON OF DASIBI PHOTOMETER WITH QAD PHOTOMETER

Comparison	Results
Initial	Dasibi = 1.01 Lab Photo. - 0.523 ppb R^2 = 0.999988
Final	Dasibi = 1.01 Lab Photo. + 2.19 ppb R^2 = 0.999952

BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"

EPA-287 (Cin.)
(4-76)

The two ultraviolet (UV) photometers (Dasibi S/N 1137 and Dasibi S/N 1141) used during the boric acid-potassium iodide (BAKI) variability study were prepared for the study by: 1) setting the span number to a value of 50.730; 2) assuring that the sample and control frequencies were in the range specified in the Dasibi instruction manual; and 3) comparing O_3 measurements made with the two photometers. Three comparisons were obtained over a 2-day period and the measurements are tabulated below (Tables G-3, G-4 and G-5). For each comparison, the least squares relationship between the two photometers is also given.

TABLE G-3. PHOTOMETER COMPARISON #1

Dasibi S/N 1137 $[O_3]$, ppm	Dasibi S/N 1141 $[O_3]$, ppm
0.4695	0.4693
0.4237	0.4235
0.3287	0.3300
0.2279	0.2269
0.1330	0.1327
0.0000	0.0000

Dasibi S/N 1141 = 1.0005 Dasibi S/N 1137 - 0.0002 ppm

TABLE G-4. PHOTOMETER COMPARISON #2

Dasibi S/N 1137 $[O_3]$, ppm	Dasibi S/N 1141 $[O_3]$, ppm
0.4600	0.4614
0.3678	0.3675
0.2727	0.2737
0.1742	0.1739
0.0773	0.0775
0.0000	0.0000

Dasibi S/N 1141 = 1.0021 Dasibi S/N 1137 - 0.0001 ppm

TABLE G-5. PHOTOMETER COMPARISON #3

Dasibi S/N 1137 $[O_3]$, ppm	Dasibi S/N 1141 $[O_3]$, ppm
0.4634	0.4630
0.3728	0.3733
0.2767	0.2767
0.1765	0.1759
0.0777	0.0774
0.0000	0.0000

Dasibi S/N 1141 = 1.0003 Dasibi S/N 1137 - 0.0002 ppm

During the field phase of the BAKI variability study, similar comparisons were obtained using a third UV photometer permanently located at Research Triangle Park (RTP), North Carolina. These comparisons were obtained before and after each trip to the field location. The third UV photometer served as a reference for these comparisons.

Chemiluminescence Ozone Analyzers

The three Bendix Model 8002 O_3 Analyzers used in the reference system were set up and calibrated using O_3 concentrations as measured with the Dasibi photometer (S/N 1137). The O_3 analyzer set-up and initial calibration data are given in Tables G-6 and G-7.

TABLE G-6. O_3 ANALYZER SET-UP

Analyzer ID	Analyzer S/N	Sample Flow (cm^3/min)	Ethylene Flow (cm^3/min)	Zero Pot Setting	Span Pot Setting
B1	26761-29	950	25.0	256	494
B2	26761-35	985	25.0	225	586
B3	26761-44	934	25.0	247	804

EPA-287 (Cin.)
(4-76)

TABLE G-7. O_3 ANALYZER CALIBRATION

$[O_3]_{\text{Dasibi Phot.}}$, ppm	O_3 Analyzer Response, % Chart B1	 B2	 B3
.0000	5.1	5.0	5.0
.0747	20.1	19.9	20.1
.1579	36.8	36.75	36.85
.2431	53.7	53.7	53.7
.3366	72.4	72.2	72.3
.4336	91.5	91.2	91.5

The initial calibration curves for the three O_3 analyzers are shown in Figures G-1, G-2, and G-3.

CONTROL SYSTEM

Ozone Generator Stability and Repeatability

The performance of the O_3 generator in the control gas phase titration (GPT) system was checked using the reference system Dasibi photometer. Four runs were obtained over the course of a day by setting the O_3 generator sleeve, allowing for a stable response and taking 10 photometer readings. The test data is tabulated below (Table G-8):

TABLE G-8. O_3 GENERATOR OUTPUT*

Run No.	SS=0	SS=3	SS=6	SS=9	SS=12	SS=14
1	.000	.086	.185	.281	.376	.438
2	.000	.087	.184	.280	.373	.433
3	.000	.087	.185	.281	.374	.434
4	.000	.087	.184	.282	.375	.434
Ave.	.000	.0868	.1845	.2810	.3745	.4348
S.D.	.000	.0005	.0006	.0008	.0013	.0022

*O_3 concentrations in ppm

Nitric Oxide Standard

The nitric oxide (NO) standard (cylinder) used in the control GPT system was a Linde NO in nitrogen standard (Cyl. #T426628). The NO content of the cylinder was assayed by direct comparison to a National Bureau of Standards (NBS), Standard Reference Material (SRM) (FF 1955, 94.33 ppm NO) using a Bendix Model 8101-C $NO/NO_2/NO_x$ Analyzer (S/N 301748-2). The assay value for the Linde cylinder was 106.8 ppm.

CHEMILUMINESCENCE OXIDES OF NITROGEN ANALYZERS

Several Bendix Model 8101-B Oxides of Nitrogen Analyzers were used during the course of the studies. Each analyzer was initially calibrated using an NBS traceable NO standard and an NBS nitrogen dioxide (NO_2) SRM. All of the analyzers exhibited linear response to NO and NO_2. The calibration data for these analyzers are given in Tables G-9 through G-12. Examples of the initial calibration curves are shown in Figures G-4 and G-5.

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3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE G-9. BENDIX NO_x ANALYZER (S/N 30307-28)

NO Calibration		NO_2 Calibration	
[NO], ppm	Analyzer Response, % Chart	[NO_2], ppm	Analyzer Response, % Chart
.0000	5.0	.0000	5.0
.0947	23.4	.1057	26.4
.2233	49.3	.1881	43.0
.3139	67.7	.2724	59.8
.3912	83.25	.3434	74.0
-	-	.4077	86.75

TABLE G-10. BENDIX NO_x ANALYZER (S/N 29671-8)

NO Calibration		NO_2 Calibration	
[NO], ppm	Analyzer Response, % Chart	[NO_2], ppm	Analyzer Response, % Chart
.0000	5.0	.000	4.9
.0947	23.8	.088	22.0
.2233	49.4	.161	36.8
.3139	67.7	.266	58.0
.3912	83.25	.399	85.0

TABLE G-11. BENDIX NO_x ANALYZER (S/N 30307-7)

NO Calibration		NO_2 Calibration	
[NO], ppm	Analyzer Response, % Chart	$[NO_2]$, ppm	Analyzer Response, % Chart
.0000	5.0	.0000	5.0
.0947	23.7	.1057	26.2
.2233	49.5	.1881	42.9
.3139	67.5	.2724	59.9
.3912	83.25	.3434	74.0
		.4077	86.5

TABLE G-12. BENDIX NO_x ANALYZER (S/N 30307-29)

NO Calibration	
[NO], ppm	Analyzer Response, % Chart
.000	5.0
.074	18.9
.158	36.0
.245	54.1
.332	71.1
.416	88.2

FLOW MEASUREMENT EQUIPMENT

The flow measurement devices used in the studies were initially certified against a spirometer maintained by the QAD. During the course of the studies, a second certification against an NBS traceable bubble flowmeter was obtained. The certification data using the two primary standards is given in Table G-13.

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3/8"
9-1/8"

EPA-287 (Cin.)
(4-76)

TABLE G-13. CERTIFICATION OF FLOW MEASUREMENT DEVICES AGAINST TWO PRIMARY STANDARDS

Flow Device	Use During Studies	Spirometer/ Flow Device	Bubble Flowmeter/ Flow Device
1 l/rev. dry-gas meter	Control GPT system ($F_O + F_D$)	1.005	1.002
3 l/rev. wet-test meter	Reference system ($F_O + F_D$)	0.9833	0.995
1 l/rev. wet-test meter	NO_2 permeation system (F_D)	0.9852	0.994

Because the certification data showed acceptable agreement within expected experimental error of the two primary standards, no correction factors were used with any of the three flow measurement devices.

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EPA-287 (Cin.)
(4-76)

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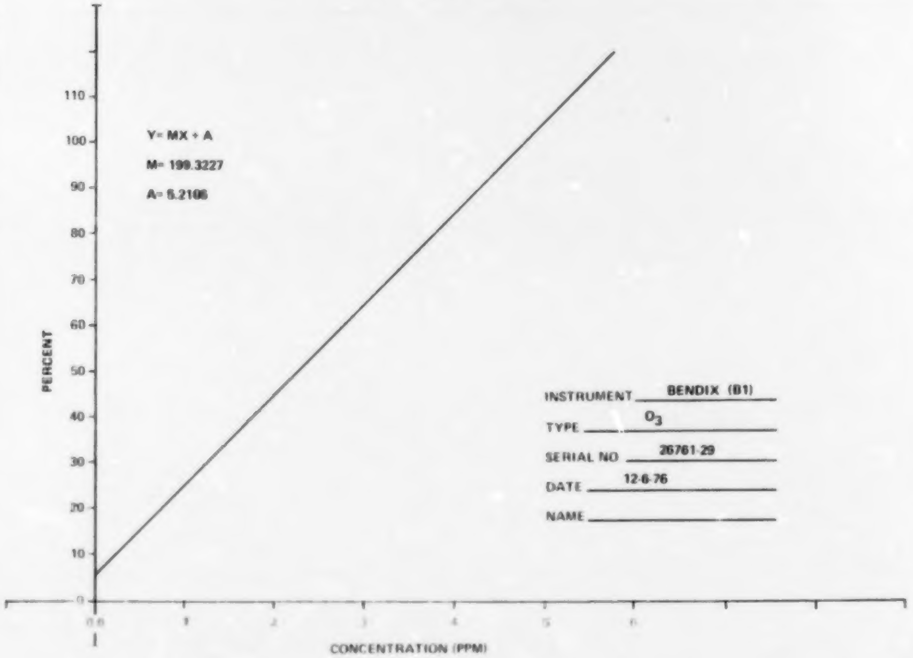

Figure G-1. Initial O_3 calibration curve (B1).

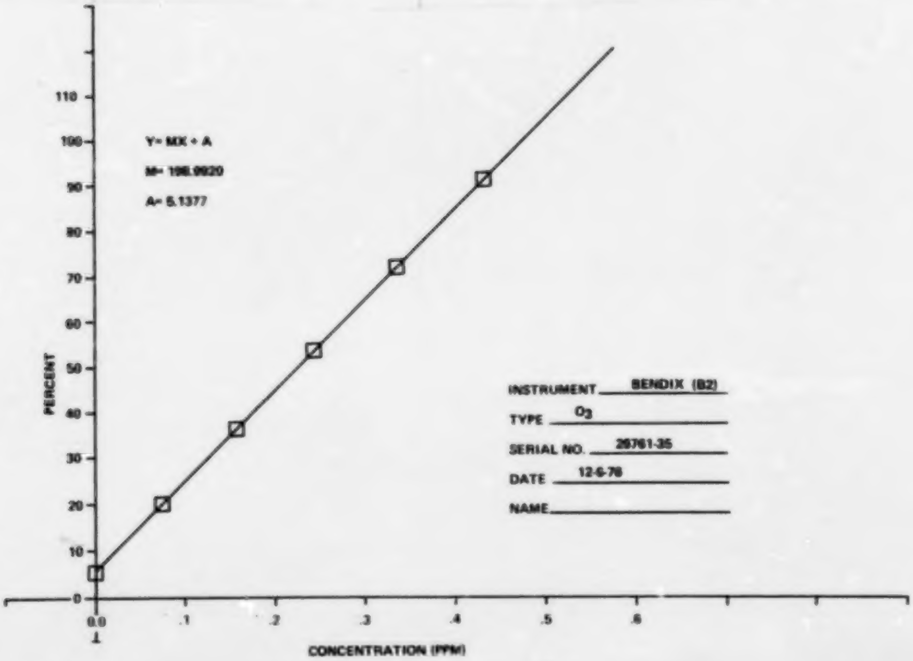

Figure G-2. Initial O_3 calibration curve (B2).

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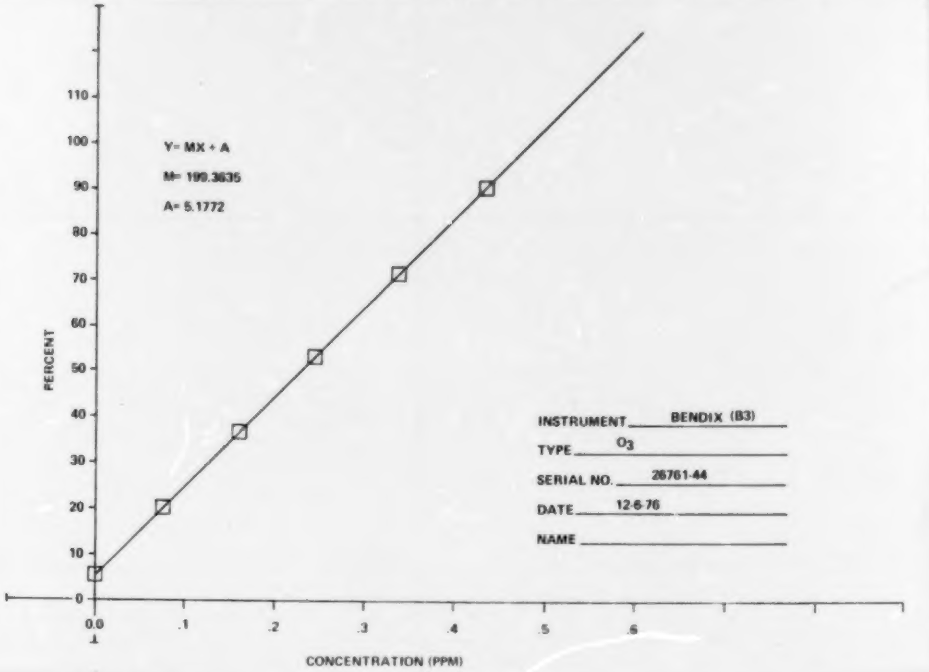
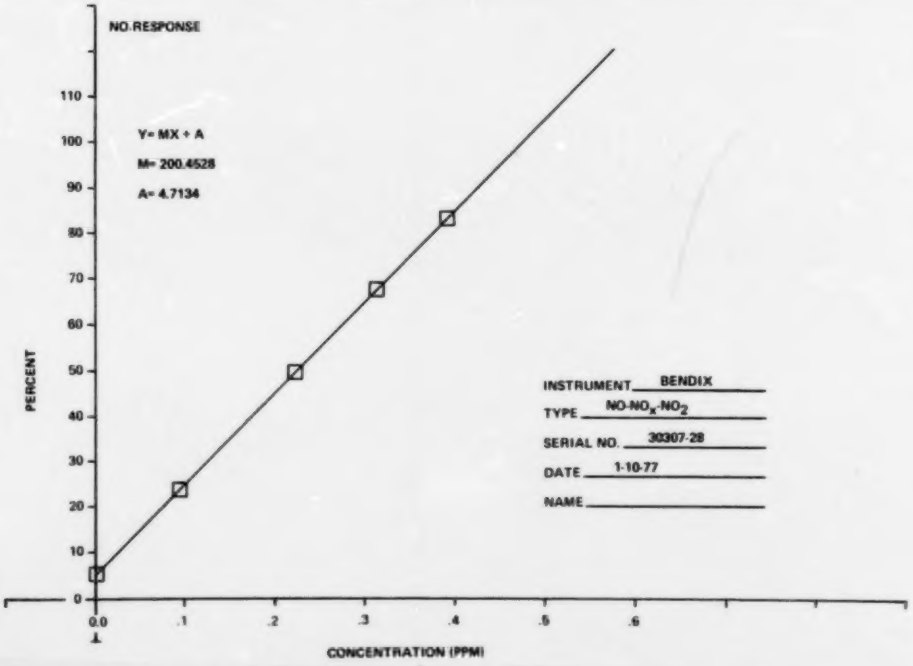
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)



INSTRUMENT BENDIX (B3)
TYPE O_3
SERIAL NO. 26761-44
DATE 12-6-76
NAME

Figure G-3. Initial O_3 calibration curve (B3).



INSTRUMENT BENDIX
TYPE $NO\text{-}NO_x\text{-}NO_2$
SERIAL NO. 30307-28
DATE 1-10-77
NAME

Figure G-4. Initial NO calibration curve.

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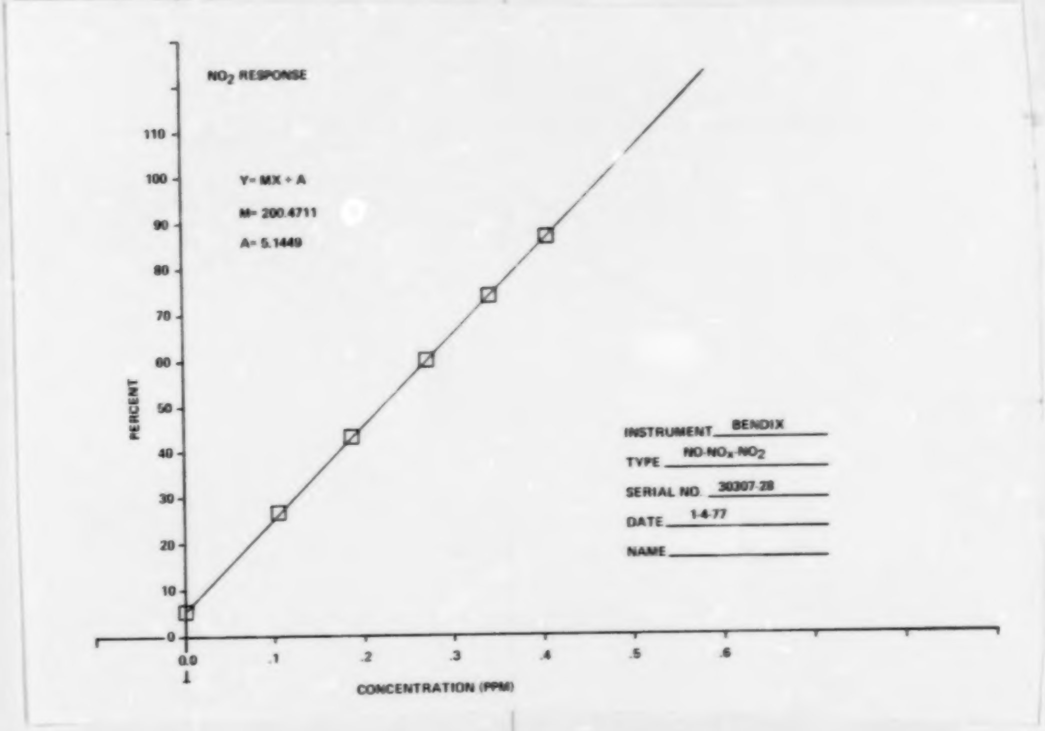
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)



INSTRUMENT BENDIX
TYPE NO-NO$_x$-NO$_2$
SERIAL NO. 30307-28
DATE 1-4-77
NAME

Figure G-5. Initial NO$_2$ calibration curve.

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3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

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9-1/8"

APPENDIX H

MISCELLANEOUS

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3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

APPENDIX H

MISCELLANEOUS

REFERENCE SYSTEM COMPONENTS

A description of the reference system components and their functions is given below. See Figure 5 of this document for a schematic representation.

Needle valves (Hoke): Control flow of zero air through O_3 generator (F_O) and zero air for ultraviolet (UV) photometer. F_O adjusted to give nominal flow rate of 1.0 l/min.

Mass flowmeter (Hastings): Monitor F_O.

Mass flow controller and mass flowmeter (Tylan): Control and monitor flow of dilution zero air (F_D). Adjusted to give nominal flow rate of 5.0 l/min.

Ozone generator (South States Industries): Generate variable O_3 concentrations by means of adjustable sleeve.

Ozone generator power supply (Ultraviolet Products): Supply power to O_3 generator.

Mixing chamber: Glass Kjeldahl bulb to provide thorough mixing of O_3 with dilution zero air.

Output manifold: Multiport glass manifold.

Wet-test meter (Precision Scientific): 3 l/rev; measurement of $F_O + F_D$.

Ultraviolet O_3 photometer - Dasibi Model 1003-AH, S/N 1137: Modified to operate as absolute photometer (O_3 scrubber removed, solenoid valve repositioned on rear panel, zero air supplied for zero portion of measurement cycle).

Chemiluminescence O_3 analyzers - Bendix Model 8002, B1-S/N 26761-29, B2-S/N 26761-35, B3-S/N 26761-44: Operated on the 0 to 0.5 ppm range.

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3/8"
PAGE NUMBER

EPA-287 (Cin.)
(4-76)

Dynamic AC line voltage regulator (California Instruments): Control of AC line voltage to O_3 generator power supply, UV O_3 photometer, and chemiluminescence O_3 analyzers.

CONTROL GAS PHASE TITRATION SYSTEM COMPONENTS

A description of the control gas phase titration (GPT) system components and their functions is given below. See Figure 11 of this document for a schematic representation.

Needle valves (Hoke): Control flow of nitric oxide (NO) from NO standard (F_{NO}) and zero air for O_3 generator (F_O) and dilution (F_D). Operator adjusted to give nominal flow rates: F_{NO} = 20 cm^3/min, F_O = 320-340 cm^3/min, F_D = 4500 cm^3/min.

Mass flowmeters (Hastings): Monitor F_O and F_D.

Ozone generator (South States Industries): Generate variable O_3 concentrations by means of adjustable sleeve.

Ozone generator power supply (Ultraviolet Products): Supply power to O_3 generator.

Constant voltage transformer (Sola): Control of AC line voltage to O_3 generator power supply.

Reaction chamber: Glass Kjeldahl bulb to provide adequate residence time for quantitative reaction of O_3 with NO.

Mixing chamber: Glass Kjeldahl bulb to provide thorough mixing of GPT reaction products with dilution zero air.

Output manifold: Multiport glass manifold.

Soap-bubble meter (Hastings): Certified 10-cm^3 and 100-cm^3 tubes; measurement of F_{NO} and F_O.

Dry-gas meter (Singer-American Meter Division): 1 l/rev; measurement of F_O + F_D.

Oxides of nitrogen analyzer - Bendix Model 8101-B: Operated on the 0 to 0.5 ppm range.

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BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

Nitric oxide standard: Linde NO in N_2, cylinder #T426628 (Assay = 106.8 ppm).

NITROGEN DIOXIDE PERMEATION SYSTEM COMPONENTS

A description of the nitrogen dioxide (NO_2) permeation system components and their functions is given below. See Figure 12 of this document for a schematic representation.

Needle valve (Hoke): Control of zero air (F_D) over NO_2 permeation tube. Adjusted to give nominal flow rate of 1.0 l/min.

Mass flowmeter (Hastings): Monitor F_D.

Water-jacketed condenser: Contain NO_2 permeation tube and ASTM thermometer.

Constant temperature bath: Temperature control of NO_2 permeation tube at 25.0° ± 0.1° C.

Thermometer (ASTM): Monitor temperature of NO_2 permeation tube.

Mixing chamber: Glass Kjeldahl bulb to provide thorough mixing of NO_2 and zero air.

Output manifold: Multiport glass manifold.

Wet-test meter (American Meter): 1 l/rev; measurement of F_D.

Nitrogen dioxide permeation tube: NBS NO_2 SRM 1629, Tube No. 1-1 (Rate = 0.754 μg/min at 25.0° C).

NITRIC OXIDE ASSAY PROCEDURE

A Bendix Model 8101-C Oxides of Nitrogen Analyzer (S/N 301748-2) operated on a nominal range of 0 to 100 ppm was used to assay the NO content of each volunteer's NO standard. The following procedure was used:

1. Measure and record analyzer response to zero air.
2. Measure and record analyzer response to two NBS SRM's. (NBS Cyl. #FF2831 - 45.2 ppm; NBS Cyl. #FF1955 - 94.33 ppm).

BOTTOM OF IMAGE AREA: OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
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3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

3. Calculate least squares slope and intercept from above measurements.
4. Measure and record analyzer response to volunteer NO standard.
5. Calculate NO content of volunteer NO standard using least squares slope and intercept relationship.

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BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

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APPENDIX I

ANALYSIS OF VARIANCE

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BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8''

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

APPENDIX I

ANALYSIS OF VARIANCE*

ANALYSIS OF VARIANCE FOR ULTRAVIOLET OZONE CALIBRATION SLOPES

TABLE I-1. ALL UV CALIBRATIONS

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	9	0.00259351	0.00028817	$\sigma_e^2 + 2\ \sigma_t^2$
Error	10	0.00011117	0.00001112	σ_e^2
Total	19	0.00270468	0.00014235	Variance ratio = 25.92
				$F_{.05}$ = 3.02

Mean = 1.0037 σ_{tot} = 0.0123

σ_e = 0.0033 reprod = 0.0341

σ_t = 0.0118 95% CI = ± 0.0278 (0.9759 to 1.0315)

TABLE I-2. DASIBI MONITORS

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	4	0.00110163	0.00027541	$\sigma_e^2 + 2\ \sigma_t^2$
Error	5	0.00008659	0.00001732	σ_e^2
Total	9	0.00118822	0.00013202	Variance ratio = 15.90
				$F_{.05}$ = 5.19

Mean = 1.0110 σ_{tot} = 0.0121

σ_e = 0.0042 reprod = 0.0335

σ_t = 0.0114 95% CI = ± 0.0336 (0.9774 to 1.0446)

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*DF: degrees of freedom
SS: sum of squares
MS: mean squares or variances

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3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

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TABLE I-3. DASIBI PHOTOMETERS

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	4	0.00043254	0.00010814	$\sigma_e^2 + 2\,\sigma_t^2$
Error	5	0.00002451	0.00000490	σ_e^2
Total	9	0.00045705	0.00005078	Variance ratio = 22.06 $F_{.05}$ = 5.19

Mean = 0.9964 σ_{tot} = 0.0075

σ_e = 0.0022 reprod = 0.0208

σ_t = 0.0072 95% CI = ± 0.0208 (0.9756 to 1.0172)

TABLE I-4. ALL UV CALIBRATIONS (Corrected to Reference Photometer)

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	9	0.00107109	0.00011901	$\sigma_e^2 + 2\,\sigma_t^2$
Error	10	0.00011124	0.00001112	σ_e^2
Total	19	0.00118233	0.00006223	Variance ratio = 10.70 $F_{.05}$ = 3.02

Mean = 1.0052 σ_{tot} = 0.0080

σ_e = 0.0033 reprod = 0.0222

σ_t = 0.0073 95% CI = ± 0.0181 (0.9871 to 1.0233)

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BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

TABLE I-5. DASIBI MONITORS (Corrected to Reference Photometer)

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	4	0.00038553	0.00009638	$\sigma_e^2 + 2\sigma_t^2$
Error	5	0.00008673	0.00001735	σ_e^2
Total	9	0.00047226	0.00005247	Variance ratio = 5.56 $F_{.05}$ = 5.19

Mean = 1.0059 σ_{tot} = 0.0076

σ_e = 0.0042 reprod = 0.0211

σ_t = 0.0063 95% CI = ± 0.0211 (0.9848 to 1.0270)

6-1/2"

TABLE I-6. DASIBI PHOTOMETERS (Corrected to Reference Photometer)

9-1/8"

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	4	0.00067562	0.00016891	$\sigma_e^2 + 2\sigma_t^2$
Error	5	0.00002451	0.00000490	σ_e^2
Total	9	0.00070013	0.00007779	Variance ratio = 34.46 $F_{.05}$ = 5.19

Mean = 1.0045 σ_{tot} = 0.0095

σ_e = 0.0022 reprod = 0.0261

σ_t = 0.0091 95% CI = 0.0261 (0.9784 to 1.0306)

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BOTTOM OF IMAGE AREA: OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

ANALYSIS OF VARIANCE FOR GAS PHASE TITRATION WITH EXCESS NITRIC OXIDE OZONE CALIBRATION SLOPES

TABLE I-7. CONTROL GPT-NO SYSTEM

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	9	0.0013574	0.0001508	$\sigma_e^2 + 2\,\sigma_t^2$
Error	10	0.0045059	0.0004506	σ_e^2
Total	19	0.0058633	0.0003086	Variance ratio = 0.3347 $F_{.05}$ = 3.02

Mean = 1.0315 σ_{tot} = 0.0212

σ_e = 0.0212   reprod = 0.0588

σ_t = 0.0000   95% CI = ± 0.0480 (0.9835 to 1.0795)

9-1/8"

TABLE I-8. VOLUNTEER GPT-NO SYSTEMS

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	9	0.0222448	0.0024716	$\sigma_e^2 + 2\,\sigma_t^2$
Error	10	0.0045452	0.0004545	σ_e^2
Total	19	0.0267900	0.0014100	Variance ratio = 5.4380 $F_{.05}$ = 3.02

Mean = 1.0741 σ_{tot} = 0.0383

σ_e = 0.0213   reprod = 0.1062

σ_t = 0.0318   95% CI = ± 0.0866 (0.9876 to 1.1608)

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3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE I-9. VOLUNTEER GPT-NO SYSTEMS (Corrected for Reference Flow and Cylinder Assay)

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	9	0.0130243	0.0014471	$\sigma_e^2 + 2\sigma_t^2$
Error	10	0.0038305	0.0003830	σ_e^2
Total	19	0.0168548	0.0008871	Variance ratio = 3.7780 $F_{.05}$ = 3.02

Mean = 1.0576 σ_{tot} = 0.0303

σ_e = 0.0196 reprod = 0.0840

σ_t = 0.0231 95% CI = ± 0.0685 (0.9891 to 1.126)

6 1/2"

ANALYSIS OF VARIANCE FOR GAS PHASE TITRATION WITH EXCESS NITRIC OXIDE NITROGEN DIOXIDE CALIBRATION SLOPES

TABLE I-10. CONTROL GPT-NO SYSTEM

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	9	0.0032617	0.0003624	$\sigma_e^2 + 2\sigma_t^2$
Error	10	0.0024924	0.0002492	σ_e^2
Total	19	0.0057541	0.0003028	Variance ratio = 1.4540 $F_{.05}$ = 3.02

Mean = 0.9892 σ_{tot} = 0.0175

σ_e = 0.0158 reprod = 0.0485

σ_t = 0.0075 95% CI = ± 0.0396 (0.9496 to 1.0288)

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EPA-287 (Cin.)
(4-76)

TABLE I-11. VOLUNTEER GPT-NO SYSTEMS

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	9	0.0107031	0.0011892	$\sigma_e^2 + 2\,\sigma_t^2$
Error	10	0.0022625	0.0002262	σ_e^2
Total	19	0.0129656	0.0006824	Variance ratio = 5.2563 $F_{.05}$ = 3.02

Mean = 1.0212 σ_{tot} = 0.0265

σ_e = 0.0150 reprod = 0.0735

σ_t = 0.0219 95% CI = ± 0.0599 (0.9613 to 1.0811)

TABLE I-12. VOLUNTEER GPT-NO SYSTEMS (Corrected for Reference Flow and Cylinder Assay)

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	9	0.0024033	0.0002670	$\sigma_e^2 + 2\,\sigma_t^2$
Error	10	0.0019705	0.0001971	σ_e^2
Total	19	0.0043738	0.0002434	Variance ratio = 1.3552 $F_{.05}$ = 3.02

Mean = 0.9902 σ_{tot} = 0.0152

σ_e = 0.0140 reprod = 0.0421

σ_t = 0.0059 95% CI = ± 0.0344 (0.9558 to 1.0246)

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3/8"
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

ANALYSIS OF VARIANCE FOR GAS PHASE TITRATION WITH EXCESS OZONE OZONE CALIBRATION SLOPES

TABLE I-13. CONTROL GPT-O_3 SYSTEM*

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	8	0.0039920	0.0004990	$\sigma_e^2 + 2\,\sigma_t^2$
Error	9	0.0010136	0.0001126	σ_e^2
Total	17	0.0050056	0.0002944	Variance ratio = 4.43 $F_{.05}$ = 3.23

Mean = 1.0236 σ_{tot} = 0.0179

σ_e = 0.0106 reprod = 0.0496

σ_t = 0.0139 95% CI = ± 0.0413 (0.9823 to 1.0649)

*Volunteer 3 not included

TABLE I-14. CONTROL GPT-O_3 SYSTEM* (Slopes Forced Through Zero)

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	8	0.0040624	0.0005078	$\sigma_e^2 + 2\,\sigma_t^2$
Error	9	0.0011553	0.0001284	σ_e^2
Total	17	0.0052177	0.0003069	Variance ratio = 3.95 $F_{.05}$ = 3.23

Mean = 1.0230 σ_{tot} = 0.0178

σ_e = 0.0113 reprod = 0.0493

σ_t = 0.0138 95% CI = ± 0.0410 (0.9820 to 1.0640)

*Volunteer 3 not included

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE I-15. VOLUNTEER GPT-O_3 SYSTEMS*

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	8	0.0615670	0.0076959	$\sigma_e^2 + 2\,\sigma_t^2$
Error	9	0.0112570	0.0012508	σ_e^2
Total	17	0.0728249	0.0042838	Variance ratio = 6.15
				$F_{.05}$ = 3.23

Mean = 1.0787 σ_{tot} = 0.0669

σ_e = 0.0354 reprod = 0.1854

σ_t = 0.0568 95% CI = ± 0.1543 (0.9244 to 1.2330)

*Volunteer 5 not included

TABLE I-16. VOLUNTEER GPT-O_3 SYSTEMS* (Slopes Forced Through Zero)

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	8	0.0613708	0.0076713	$\sigma_e^2 + 2\,\sigma_t^2$
Error	9	0.0101637	0.0011293	σ_e^2
Total	17	0.0715345	0.0042079	Variance ratio = 6.79
				$F_{.05}$ = 3.23

Mean = 1.0811 σ_{tot} = 0.0663

σ_e = 0.0336 reprod = 0.1838

σ_t = 0.0572 95% CI = ± 0.1529 (0.9282 to 1.2340)

*Volunteer 5 not included

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EPA-287 (Cin.)
(4-76)

TABLE I-17. VOLUNTEER GPT-O_3 SYSTEMS* (Corrected for Reference Flow and Cylinder Assay)

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	8	0.0182568	0.0022821	$\sigma_e^2 + 2\,\sigma_t^2$
Error	9	0.0117411	0.0013046	σ_e^2
Total	17	0.0299979	0.0013046	Variance ratio = 1.75 $F_{.05}$ = 3.23

Mean = 1.0880 σ_{tot} = 0.0423

σ_e = 0.0361 reprod = 0.1172

σ_t = 0.0221 95% CI = ± 0.0977 (0.9903 to 1.1857)

*Volunteer 5 not included

ANALYSIS OF VARIANCE FOR BORIC ACID-POTASSIUM IODIDE OZONE CALIBRATION SLOPES*

TABLE I-18. BAKI CALIBRATIONS AT RTP

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	8	0.0532381	0.0066548	$\sigma_e^2 + 2\,\sigma_t^2$
Error	9	0.0027533	0.0003059	σ_e^2
Total	17	0.0559914	0.0032936	Variance ratio = 21.75 $F_{.05}$ = 3.23

Mean = 0.9769 σ_{tot} = 0.0590

σ_e = 0.0175 reprod = 0.1635

σ_t = 0.0563 95% CI = ± 0.1361 (0.8408 to 1.1130)

*Volunteer 6 not included

EPA-287 (Cin.)
(4-76)

TABLE I-19. BAKI CALIBRATIONS AT RTP (Slopes Forced Through Zero)

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	8	0.0426848	0.0053356	$\sigma_e^2 + 2\,\sigma_t^2$
Error	9	0.0049258	0.0005473	σ_e^2
Total	17	0.0476106	0.0028006	Variance ratio = 9.75 $F_{.05}$ = 3.23

Mean = 0.9744 σ_{tot} = 0.0542

σ_e = 0.0234 reprod = 0.1503

σ_t = 0.0489 95% CI = ± 0.1250 (0.8494 to 1.0994)

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TABLE I-20. BAKI CALIBRATIONS AT RTP (Corrected for I_2 Molar Absorptivity)

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	8	0.0300891	0.0037611	$\sigma_e^2 + 2\,\sigma_t^2$
Error	9	0.0028158	0.0003129	σ_e^2
Total	17	0.0329049	0.0019356	Variance ratio = 12.02 $F_{.05}$ = 3.23

Mean = 0.9906 σ_{tot} = 0.0451

σ_e = 0.0177 reprod = 0.1250

σ_t = 0.0415 95% CI = ± 0.1040 (0.8866 to 1.0946)

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EPA-287 (Cin.)
(4-76)

TABLE I-21. ALL BAKI CALIBRATIONS

Source	DF	SS	MS	Estimate of Mean Sum
Treatment	11	0.0629886	0.0057262	$\sigma_e^2 + 2\ \sigma_t^2$
Error	12	0.0056247	0.0004687	σ_e^2
Total	23	0.0686133	0.0029832	Variance ratio = 12.22 $F_{.05}$ = 2.72

Mean = 0.9865 σ_{tot} = 0.0557

σ_e = 0.0216 reprod = 0.1544

σ_t = 0.0513 95% CI = ± 0.1226 (0.8639 to 1.1091)

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